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Some Generating Functions of Appell—Function F_1

By

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Abstract

In this paper we give some generating functions for the Appell function F_1.

1. Introduction

The object of this paper is to prove some new generating functions for the Appell Function F_1.

We require the following formulae in our investigation :

We have [2, p. 268]

$$(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}=\sum_{n=0}^{\infty}\binom{\lambda}{n}F_1[-n\,;-\mu,-\gamma\,;\lambda-n+1\,;x,y]t^n \tag{1}$$

[1, p. 239]

$$F_1[\alpha\,;\beta,\beta';\gamma\,;x,1]=\frac{\Gamma(\gamma)\,\Gamma(\gamma-\alpha-\beta')}{\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta')}\,{}_2F_1(\alpha,\beta\,;\gamma-\beta'\,;x) \tag{2}$$

$$F_1[\alpha\,;\beta,\beta';\gamma\,;x,x]={}_2F_1(\alpha,\beta+\beta';\gamma\,;x) \tag{3}$$

$$F_1[\alpha\,;\beta,\beta';\gamma\,;x,y]=(1-x)^{-\beta}(1-y)^{-\beta'}F_1\left[\gamma-\alpha\,;\beta,\beta';\gamma\,;\frac{x}{x-1},\frac{y}{y-1}\right] \tag{4}$$

[5, p. 254]

$$P_n^{(\alpha,\beta)}(x)=\frac{(1+\alpha)_n}{n\,!}\,{}_2F_1\left(-n,1+\alpha+\beta+n\,;1+\alpha\,;\frac{1-x}{2}\right) \tag{5}$$

2. The first formula to be proved is

$$\sum_{n=0}^{\infty}\binom{\lambda}{m+n}\binom{m+n}{n}F_1[-n-m\,;-\mu,-\gamma\,;\lambda-n-m+1\,;x,y]\,t^n$$

$$= (1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\frac{(-\gamma)_m}{m!}\left(\frac{-\gamma}{1+yt}\right)^m,$$

$$F_1\left[-m;-\lambda,-\mu;1+\gamma-m;\frac{1+yt}{y(1+t)},\frac{x(1+yt)}{y(1+xt)}\right]. \tag{6}$$

Proof: We consider the series

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\binom{\lambda}{n+m}F_1[-n-m;-\mu,-\gamma;\lambda-n-m+1;x,y]\binom{n+m}{n}t^n v^m$$

$$=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\binom{\lambda}{n}F_1[-n;-\mu,-\gamma;\lambda-n+1;x,y]\binom{n}{m}t^{n-m}v^m$$

$$=\sum_{n=0}^{\infty}\binom{\lambda}{n}F_1[-n;-\mu,-\gamma;\lambda-n+1;x,y](t+v)^n$$

$$=[1+t+v]^{\lambda}[1+x(t+v)]^{\mu}[1+y(t+v)]^{\gamma} \quad \text{by (1)}$$

$$=(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\left[1+\frac{v}{1+t}\right]^{\lambda}\left[1+\frac{vx}{1+xt}\right]^{\mu}\left[1+\frac{vy}{1+yt}\right]^{\gamma}$$

$$=(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\sum_{p,q,r=0}^{\infty}\frac{(-\gamma)_p(-\mu)_q(-\gamma)_r}{p!\,q!\,r!}\left[\frac{-v}{1+t}\right]^p\left[\frac{-vx}{1+xt}\right]^q\left[\frac{-vy}{1+yt}\right]^r$$

$$=(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\sum_{p,q=0}^{\infty}\sum_{m=0}^{\infty}\frac{(-m)_{p+q}(-\lambda)_p(-\mu)_q}{(1+\gamma-m)_{p+q}\,p!\,q!}\left[\frac{1+yt}{y(1+t)}\right]^p\left[\frac{x(1+yt)}{y(1+xt)}\right]^q$$
$$\frac{(-\gamma)_m}{m!}\left(\frac{-y}{1+yt}\right)^m v^m$$

$\therefore$ Equating the coefficients of v^m on both sides we get,

$$\sum_{n=0}^{\infty}\binom{\lambda}{n+m}\binom{m+n}{n}F_1[-n-m;-\mu,-\gamma;\lambda-n-m+1;x,y]t^n$$

$$=(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\frac{(-\gamma)_m}{m!}\left(\frac{-y}{1+yt}\right)^m$$

$$F_1\left[-m;-\lambda,-\mu;1+\gamma-m;\frac{1+yt}{y(1+t)},\frac{x(1+yt)}{y(1+xt)}\right]$$

This completes the proof of (6).

In particular if we put $m=0$ in (6) we get (1).

In case we put $y=x$ in (6) we get

$$\sum_{n=0}^{\infty}\binom{\lambda}{n+m}\binom{m+n}{n}{}_2F_1[-n-m,-\mu-\gamma;\lambda-n-m+1;x]\,t^n$$

$$= (1 + t)^{\lambda} (1 + xt)^{\mu+\gamma} \frac{(-\mu-\gamma)_m}{m!} \left(\frac{-x}{1+xt}\right)^m {}_2F_1\left[\begin{matrix}-m, -\lambda ; & \frac{1+xt}{x(1+t)}\\ 1+\mu+\gamma-m ; & \end{matrix}\right] \quad (7)$$

by using (2) and (3)

3. The second formula to be proved is

$$\sum_{n=0}^{\infty} \frac{(-\lambda)_{n+m}}{(n+m)!} F_1[-n-m ; -\mu, -\gamma ; \lambda-n-m+1 ; x, y] t^n$$

$$= \frac{(-\lambda)_m}{m!} (1-x)^{\mu} (1-y)^{\gamma} H_2\left[1+\lambda ; -\mu, -\gamma, 1 ; 1+\lambda-m, 1+m ; \frac{x}{x-1}, \frac{y}{y-1}, -t\right] \quad (8)$$

where $H_2\left[1+\lambda ; -\mu, -\gamma, 1 ; 1+\lambda-m, 1+m ; \frac{x}{x-1}, \frac{y}{y-1}, -t\right]$

$$= \sum_{p,q,r=0}^{\infty} \frac{(1+\lambda)_{p+q} (-\mu)_p (-\gamma)_q (1)_r}{(1+\lambda-m)_{p+q-r} (1+m)_r} \frac{\left(\frac{x}{x-1}\right)^p \left(\frac{y}{y-1}\right)^q (-t)^r}{p!\, q!\, r!}$$

Proof: By using (4) in the left member of (8) we get

$$(1-x)^{\mu} (1-y)^{\gamma} \frac{(-\lambda)_m}{m!} \sum_{n=0}^{\infty} \frac{(m\ \lambda)_n (1)_n}{(1+m)_n\, n!} t^n F_1\left[1+\lambda ; -\mu, -\gamma ; 1+\lambda-n-m ; \frac{x}{x-1}, \frac{y}{y-1}\right]$$

$$= \frac{(-\lambda)_m}{m!} (1-x)^{\mu} (1-y) \sum_{n=0}^{\infty} \frac{(m-\lambda)_n (1)_n}{(1+m)_n\, n!} t^n \sum_{p,q=0}^{\infty} \frac{(1+\lambda)_{p+q} (-\mu)_p (-\gamma)_q}{(1+\lambda-n-m)_{p+q}\, p!\, q!} \left(\frac{x}{x-1}\right)^p \left(\frac{y}{y-1}\right)^q$$

$$= \frac{(-\lambda)_m}{m!} (1-x)^{\mu} (1-y)^{\gamma} \sum_{p,q,n=0}^{\infty} \frac{(1+\lambda)_{p+q} (-\mu)_p (-\gamma)_q (1)_n}{(1+\lambda-m)_{p+q-n} (1+m)_n} \frac{\left(\frac{x}{x-1}\right)^p \left(\frac{y}{y-1}\right)^q (-t)^n}{p!\, q!\, n!}$$

$$= \frac{(-\lambda)_m}{m!} (1-x)^{\mu} (1-y)^{\gamma} H_2\left[1+\lambda ; -\mu, -\gamma, 1 ; 1+\lambda-m ; 1+m ; \frac{x}{x-1}, \frac{y}{y-1} -t\right]$$

which completes the proof of (8).

Again putting $m = 0$ in (8) we get our result (1).

4. The third formula to be proved is

$$\sum_{k=0}^{n} \binom{\lambda}{n-k} \binom{\lambda}{k} F_1[-n+k ; -\mu, -\gamma ; \lambda-n+k+1 ; x, y] F_1[-k ; -\mu', -\gamma' ; \lambda'-k+1, x, y]$$

$$= \binom{\lambda+\lambda'}{n} F_1[-n ; -\mu-\mu', -\gamma-\gamma' ; \lambda+\lambda'-n+1, x, y]. \quad (9)$$

Proof: By (1) we have

$$\sum_{n=0}^{\infty} \binom{\lambda+\lambda'}{n} F_1[-n ; -\mu-\mu', -\gamma-\gamma' ; \lambda+\lambda'-n+1 ; x, y] t^n$$

$$= [(1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}][(1+t)^{\lambda'}(1+xt)^{\mu'}(1+yt)^{\gamma'}]$$

$$= \sum_{n=0}^{\infty}\binom{\lambda}{n} F_1[-n; -\mu, -\gamma; \lambda-n+1; x, y]\, t^n \sum_{k=0}^{\infty}\binom{\lambda'}{k} F_1(-k; -\mu', -\gamma'; \lambda'-k+1; x, y]\, t^k$$

$$= \sum_{n=0}^{\infty}\sum_{k=0}^{n}\binom{\lambda}{n-k} F_1[-n+k; -\mu, -\gamma; \lambda-n+k+1, x, y]\binom{\lambda'}{k}$$

$$F_1[-k, -\mu', -\gamma'; \lambda'-k+1, x, y]\, t^n$$

$\therefore$ Equating the coefficients of t^n on both sides we get (9)

In particular if we put $y = x$ in (9) we get

$$\sum_{k=0}^{n}\binom{\lambda}{n-k}\binom{\lambda'}{k}\, {}_2F_1[-k, -\mu'-\gamma'; \lambda'-k+1; x]\, {}_2F_1[-n+k, -\mu-\gamma; \lambda-n+k+1; x]$$

$$= \binom{\lambda+\lambda'}{n}\, {}_2F_1[-n, -\mu-\mu'-\gamma-\gamma'; \lambda+\lambda'-n+1; x] \tag{10}$$

by using (3)

If we put $y = 1$, in (9) we get

$$\sum_{k=0}^{n}\binom{n}{k}(-\lambda-\gamma)_{n-k}(-\lambda'-\gamma')_k\, {}_2F_1\left[\begin{matrix}-n+k, -\mu;\\ 1+\lambda+\gamma-n+k;\end{matrix}\ x\right]{}_2F_1\left[\begin{matrix}-k, -\mu';\\ 1+\lambda'+\gamma'-k;\end{matrix}\ x\right]$$

$$= (-\lambda-\lambda'-\gamma-\gamma')_n\, {}_2F_1[-n, -\mu-\mu'; 1+\lambda+\lambda'+\gamma+\gamma'-n; x) \tag{11}$$

by using (2).

5. The fourth formula to be proved is

$$\sum_{n=0}^{\infty}\binom{\lambda}{n} F_1[-n; -\mu, -\gamma; \lambda-n+1; x, y]\, F_1[\delta; -n, \alpha; \beta; z, wz]\, t^n$$

$$= (1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma} F_D\left[\delta; -\lambda, -\mu, -\gamma, \alpha; \quad ; \frac{tz}{1+t}, \frac{xtz}{1+xt}, \frac{ytz}{1+yt}, wz\right] \tag{12}$$

For Lauricella's function F_D see [3]

Proof: Expanding the second F_1 in left-member of (12) we get

$$\sum_{n=0}^{\infty}\binom{\lambda}{n} F_1[-n; -\mu, -\gamma; \lambda-n+1; x, y]\, t^n \sum_{p=0}^{n}\sum_{q=0}^{\infty}\frac{(\delta)_{p+q}}{(\beta)_{p+q}}\frac{(-n)_p}{p!}\frac{(\alpha)_q}{q!}, z^p (wz)^q$$

$$= \sum_{p,q=0}^{\infty}\frac{(\delta)_{p+q}(\alpha)_q}{(\beta)_{p+q}\, q!}(-tz)^p (wz)^q \sum_{n=0}^{\infty}\binom{\lambda}{n+p}\binom{n+p}{n} F_1[-n-p; -\mu, -\gamma; \lambda-n-p+1, x, y]\, t^n$$

$$= (1+t)^{\lambda}(1+xt)^{\mu}(1+yt)^{\gamma}\sum_{p,q=0}^{\infty}\frac{(\delta)_{p+q}(\alpha)_q}{(\beta)_{p+q}\, q!}(-tz)^p (wz)^q \frac{(-\gamma)_p}{p!}\left(\frac{-y}{1+yt}\right)^p$$

$$F_1\left[[-p\,;-\lambda,-\mu\,;\,1+\gamma-p\,;\,\frac{1+yt}{y(1+t)}\,,\,\frac{x(1+yt)}{y(1+xt)}\right] \text{ by (6)}$$

$$= (1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma \sum_{p,q,r,s=0}^{\infty} \frac{(\delta)_{p+q}\,(-\gamma)_p\,(\alpha)_q\,(-p)_{r+s}\,(-\lambda)_r\,(-\mu)_s}{(\beta)_{p+q}\,(1+\gamma-p)_{r+s}\,p!\,q!\,r!\,s!}$$

$$\left[\frac{ytz}{1+yt}\right]^p (wz)^q \left[\frac{1+yt}{y(1+t)}\right]^r \left[\frac{x(1+yt)}{y(1+xt)}\right]^s$$

$$= (1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma \sum_{p,q,r,s=0}^{\infty} \frac{(\delta)_{p+q+r+s}\,(-\lambda)_r\,(-\mu)_s\,(-\gamma)_p\,(\alpha)_q}{(\beta)_{p+q+r+s}\,r!\,s!\,p!\,q!}$$

$$\left[\frac{tz}{1-t}\right]^r \left[\frac{xtz}{1+xt}\right]^s \left[\frac{ytz}{1+yt}\right]^p (wz)^q$$

$$= (1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma\,F_D\left[+\delta\,;-\lambda,-\mu,-\gamma,\alpha\,;\,\beta\,;\,\frac{tz}{1+t},\,\frac{xtz}{1+xt},\,\frac{ytz}{1+yt},\,wz\right].$$

This completes the proof of (11)

In particular if we put $w = 1$ in (11) we get by (3).

$$\sum_{n=0}^{\infty}\binom{\lambda}{n} F_1[-n\,;-\mu,-\gamma\,;\,\lambda-n+1\,;\,x,y]\;{}_2F_1(\delta,-n+\alpha\,;\,\beta\,;\,z)\,t^n$$

$$(1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma\quad F_D\left[\delta\,;-\lambda,-\mu,-\gamma,\alpha\,;\,\beta\,;\,\frac{tz}{1+t},\,\frac{xtz}{1+xt},\,\frac{ytz}{1+yt},\,z\right]$$

Now putting ${}_2F_1$ in L.H.S. as a Jacobi polynomial by (5) and replacing α by $-m$, $\beta-1$ by α, $\delta-\beta$ by β, z by $\frac{1-z}{2}$ we get

$$\sum_{n=0}^{\infty}\frac{(m+n)!}{(1+\alpha)_{m+n}}\binom{\lambda}{n} P_{m+n}^{(\alpha,\,\beta-m-n)}(z)\,F_1[-n\,;-\mu,-\gamma\,;\,\lambda-n+1\,;\,x,y]\,t^n$$

$$= (1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma\,F_D\Big[1+\alpha+\beta\,;-\lambda,-\mu,-\gamma,-m\,;\,1+\alpha\,;$$

$$\frac{t(1-z)}{2(1+t)},\,\frac{xt(1-z)}{2(1+xt)},\,\frac{yt(1-z)}{2(1+yt)},\,\frac{1-z}{2}\Big] \tag{13}$$

In particular if we put $m = 0$ in (13) we get

$$\sum_{n=0}^{\infty}\frac{n!}{(1+\alpha)_n}\binom{\lambda}{n} P_n^{(\alpha,\,\beta-n)}(z)\;F_1[-n\,;-\mu,-\gamma\,;\,\lambda-n+1\,;\,x,y]\,t^n$$

$$(1+t)^\lambda\,(1+xt)^\mu\,(1+yt)^\gamma\,F_D\Big[1+\alpha+\beta\,;-\lambda,-\mu,-\gamma\,;\,1+\alpha\,;$$

$$\frac{t(1-z)}{2(1+t)},\,\frac{xt(1-z)}{2(1+xt)},\,\frac{yt(1-z)}{2(1+yt)}\Big] \tag{14}$$

If we put $x = y = 0$ in (13) and replace λ by $-\lambda$, t by $-t$ and transform the F_1 in R. H. S. by (4) we get

$$\sum_{n=0}^{\infty} \frac{(m+n)}{n!} \frac{(\lambda)_n}{(1+\alpha)_{m+n}} t^n P_{m+n}^{(\alpha,\, \beta-m-n)}(z) = \left(\frac{z+1}{2}\right)^m \left[1-t\left(\frac{z+1}{2}\right)\right]^{-\lambda}$$

$$F_1\left[-\beta\,;\, \lambda, -m\,;\, 1+\alpha\,;\, \frac{t(1-z)}{2-t(z+1)}, \frac{z-1}{z+1}\right] \tag{15}$$

which is the result due to Manocha and Sharma [4].

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Kinetics of Oxidation of Morpholine by Potassium Peroxydisulphate

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Abstract

Kinetics of uncatalysed oxidation of morpholine by peroxydisulphate has been studied by measuring the rate of disappearance of peroxydisulphate iodometrically. The reaction is of second order, being first order each with respect to morpholine and peroxydisulphate respectively. Sodium sulphate and potassium sulphate have no effect on the rate of uncatalysed oxidation. Copper sulphate slightly and silver nitrate markedly accelerate the rate of oxidation and the rate of oxidation is directly proportional to the concentration of $AgNO_3$. Energy of activation, frequency factor, entropy factor, and entropy of activation have been calculated.

Introduction

Studies on the kinetics of oxidation of organic nitrogen compounds by peroxydisulphate have received little attention and only a few kinetics investigations in this field have been reported.[1] Beileryan[2] and coworkers have studied the oxidation of some amines and aminoalcohols. Agrawal and Mushran[3] have studied the kinetics of silver-ion catalysed oxidation of urea and acetamide. As no systematic study of the kinetics of oxidation of Morpholine by peroxydisulphate has been made so far, the present authors have undertaken this investigation and the results of such a study are presented in this paper.

Preliminary study indicated that the reaction between morpholine and peroxydisulphate proceeds at a measurable speed at ordinary temperature even in the absence of silver-ions. Bisht and Srivastava[4] have reported in their study of the salt effect in silver catalysed oxidation of oxalic by peroxydisulphate that the iodometric method of Szabo[5] *et al* is not suitable for the estimation of persulphate as the low concentration of 0·005 M employed in their study. Bartlett and Cotman Jr[6] estimated persulphate by a modification of the method recommended by Rosin. Allen[7] estimated persulphate by a modification of Bartlett and Cotmans' procedure. The present authors have found that the method recommended by Kolthoff and Carr[8] with a slight modification is suitable for estimation of peroxydisulphate in the present study. The slight modification consists in adding 2 ml. of 6N acetic acid to 10 ml. of 40% KI solution taken in a flask just before pipetting out aliquot portion of the reaction mixture in the same flask and allowing it to stand for 20 minutes and then titrating the liberated iodine with standard hypo solution. The advantage of this modification is that it aids in 'quenching' the reaction between morpholine and peroxydisulphate by converting morpholine (which behaves like an aliphatic amine) into the unreactive species (Morp. H^+) and all the unreacted peroxydisulphate liberates iodine.

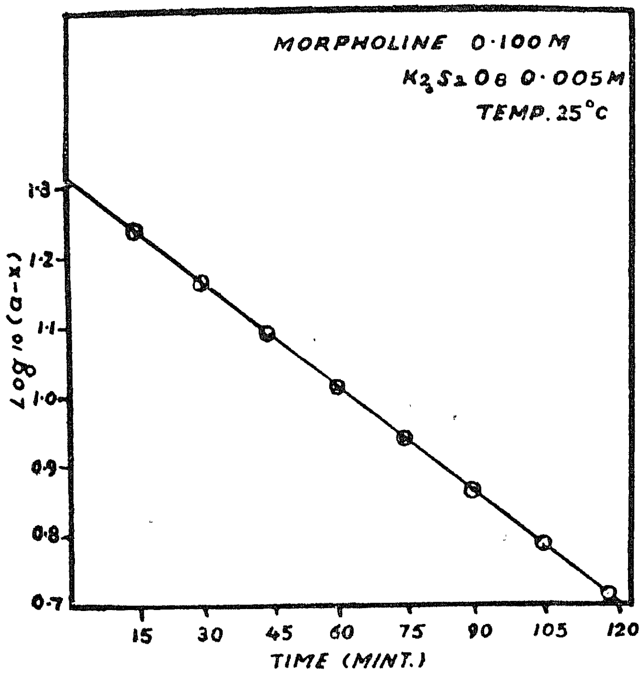
MORPHOLINE 0·100 M
$K_2S_2O_8$ 0·005M
TEMP. 25°C
$Log_{10}(a-x)$
TIME (MINT.)

Fig.1

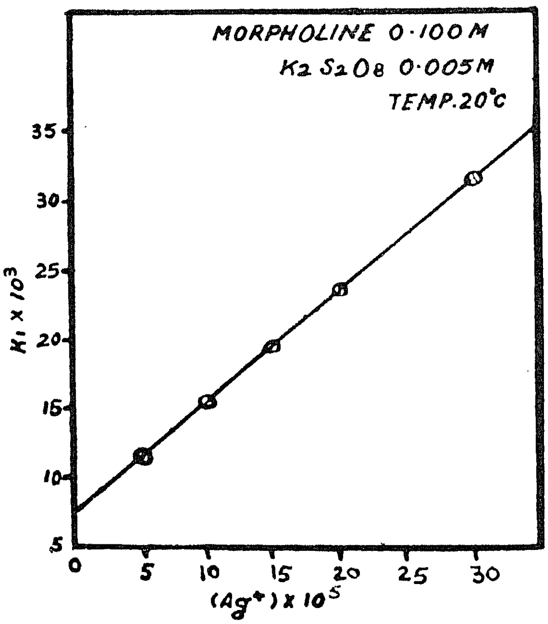
MORPHOLINE 0·100 M
$K_2S_2O_8$ 0·005M
TEMP. 20°C
$K_1 \times 10^3$
$(Ag^+) \times 10^5$

Fig.2

Experimental

All the chemicals used were of A. R. quality. Solutions were prepared by direct weighing.

Measured amount of morpholine was pipetted out in a reaction flask and kept in the thermostat maintained at the required reaction temperature. Solution of potassium peroxydisulphate was suspended in the other flask at the same temperature. After allowing sufficient time for the reactants to attain the temperature of the bath, requisite amount of potassium peroxydisuphate solution was pipetted out in the reaction flask to start the reaction. 10 ml. aliquots of reaction mixture were taken out at suitable intervals of time and added to the flask containing 10 ml. of 40% KI and 2 ml. of 6N acetic acid. The flask was allowed to stand for 20 minutes and then the liberated iodine was titrated with standard thiosulphate solution using starch indicator.

Determination of order of reaction

The order of reaction with respect to peroxydisulphate was found out by Ostwald's isolation method. The concentration of morpholine was taken in excess so that its concentration essentially remains almost constant throughout the course of reaction. The pseudo first order constant was calculated by the equation :

$$K_1 = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x}$$

and the data for one such experiment are presented in Table 1.

TABLE I

Temperature 25°C

Overall concentration

Morpholine 0·100 M
Potassium peroxydisulphate 0·005 M

Time in minutes	Vol. of hypo (a–x) ml.	$K_1 \times 10^2$ min.$^{-1}$
0	20·30	–
15	17·20	1·105
30	14·60	1·098
45	12·30	1·114
60	10·30	1·131
75	8·70	1·130
90	7·30	1·137
105	6·05	1·153
120	5·10	1·152
	Average	1·127

The plot of $\log_{10}$ (a-x) against time was linear (Fig. 1). This shows that the order of reaction with respect to peroxydisulphate is one.

The order of reaction with respect to morpholine was determined by using the expression

$$n = \frac{\log\left(\frac{K_1'}{K_1''}\right)}{\log\left(\frac{C_1}{C_2}\right)}$$ where K_1' and K_1''

are the pseudo first order rate constants at two different excess concentrations C_1 and C_2 of morpholine respectively. The values of n are recorded in Table 2.

TABLE 2

Temperature 25°C

C_1	C_2	$K_1' \times 10^2$	$K_1'' \times 10^2$	n
0·10 M	0·05M	1·127	0·5631	1·001
0·20 M	0·10M	2·288	1·127	1·021
0·20 M	0·05M	2·288	0·5631	1·011

It is quite clear from table 2 that the order of reaction with respect to morpholine is one.

The total order of reaction is thus found to be two, being one with respect to each. The values of second order rate constants were obtained by dividing the pseudo first order rate constants by the actual concentration of morpholine and the results at different temperatures are given in Table 3.

TABLE 3

Temperature °C	Conc. of morpholine (M)	First order $K_1 \times 10^2$ min.$^{-1}$	Second order $K_s \times 10^2$ lit. mole^{-1} min.$^{-1}$
20	0·1	0·7159	7·152
20	0·2	1·436	7·18
25	0·05	0·5631	11·262
25	0·1	1·127	11·27
25	0·2	2·288	11·44
30	0·1	1·79	17·90
30	0·2	3·496	17·48
35	0·1	2·724	27·24

Table 3 clearly shows that the values of second order rate constant K_s at any one particular temperature are fairly constant.

Effect of Salts

The effect of adding salts sodium sulphate and potassium sulphate on the rate of oxidation is presented in table 4.

TABLE 4

Morpholine 0·20 M ; Potassium peroxydisulphate 0·005M
Temperature 25°C

Salt	Concentration (M)	$K_1 \times 10^2$ min.$^{-1}$
–	–	2·288
Potassium sulphate	0·005	2·26
Potassium sulphate	0·02	2·199
Potassium sulphate	0·08	2·228
Sodium sulphate	0·02	2·295
Sodium sulphate	0·04	2·287
Sodium sulphate	0·08	2·258

There is no significant change on the rate of uncatalysed oxidation on the addition of the above salts.

Effect of copper sulphate and silver nitrate

The effect of adding copper sulphate and silver nitrate on the rate of oxidation are recorded in table 5.

TABLE 5

Temperature 20°C. Morpholine 0·10 M.
Potassium peroxydisulphate 0·005 M

Substance added	Concentration (M)	$K_1 \times 10^2$ min.$^{-1}$
–	–	0·7159
$CuSO_4\ 5H_2O$	10×10^{-5}	0·8445
$CuSO_4\ 5H_2O$	30×10^{-5}	0·8766
$AgNO_3$	5×10^{-5}	1·139
$AgNO_3$	10×10^{-5}	1·538
$AgNO_3$	15×10^{-5}	1·934
$AgNO_3$	20×10^{-5}	2·349
$AgNO_3$	30×10^{-5}	3·132

A perusal of table 5 shows that at similar concentrations of $CuSO_4 5H_2O$ and $AgNO_3$, the Cu^{++} ions accelerate the rate of oxidation slightly whereas Ag^+ ions accelerate the rate very markedly. It is further found that the relationship between the $[Ag^+]$ and K_1 is linear (Fig. 2). A plot of K_1 against $[Ag^+]$ yields a straight line and the value of K_1 read from the graph at zero $[Ag^+]$ is found to be nearly equal to 0·7159 determined experimentally.

The energy of activation, frequency factor, entropy factor and entropy of activation for the uncatalysed oxidation are found to be 16100 cals./mole, $1{\cdot}185\times10^9$ litres mole^{-1} sec.$^{-1}$, $7{\cdot}023\times10^{-5}$ and $-19{\cdot}01$ e.u. respectively.

Discussion

As the uncatalysed reaction is second order, being first order with respect to each reactant, the rate of disappearance of peroxydisulphate is given by the expression :

$$-d\,[S_2O_8^{-2}]\,/\,dt = K_s\,[\text{Morpholine}]\,[S_2O_8^{-2}]$$

The probable mechanism of uncatalysed oxidation of morpholine is :

$$\text{Morpholine} + S_2O_8^{-2} \xrightarrow{\text{slow}} (\text{Morp. } S_2O_8)^{-2} \text{ rate determining}$$

$$(\text{Morp. } S_2O_8)^{-2} + H_2O \xrightarrow{\text{fast}} (\text{Morp.O}) + 2HSO_4^{-} + \text{other oxidation products.}$$

An oxidation product in the case of morpholine is the oxime as qualitative test for this group in the reaction mixture indicates the presence of oxime.

Acknowledgements

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Periodic Precipitation of Cadmium Sulphide

By

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Abstract

The Liesegang rings of cadmium sulphide are observed in all the three gel media *viz.* gelatin, agar agar and starch. In the gelatin and starch media both 'Direct' and 'Revert' type of rings are obtained. In agar agar media only 'Direct' type of rings are formed.

Introduction

A review of the literature shows that the formation of Liesegang rings of cadmium sulphide in gelatin medium has been reported by Hastchek[1] and Dhar and Chatterjee[2]. The periodic precipitation of cadmium sulphide has not been reported in agar agar and starch media. During the studies of periodic precipitation of cadmium sulphide in the gelatin gel it has been observed by us that when Cadmium sulphate solution is allowed to diffuse in gel containing Sodium sulphide, 'Revert' type of rings are obtained and 'Direct' type of rings are formed when sodium sulphide solution is allowed to diffuse in the gelatin gel containing cadmium sulphate. We have also obtained the Liesegang rings of cadmium sulphide in agar agar and starch gels.

Experimental

The formation of the periodic precipitate of cadmium sulphide in gelatin gel is presented in the following tables :

TABLE I

Concentration of cadmium sulphate solution diffusing from the top – 0·04 M

Number of rings	Concentration of sodium sulphide in 6% gelatin gel		
	0·04 M	0·02 M	0·01 M
	0 cms.	0 cms.	0 cms.
1	0·92	1·43	No rings
2	1·24	1·77	
3	1·44	1·99	
4	1·62	2·17	
5	1·73	2·35	
6	1·83	2·51	
7	1·92	2·67	
8	2·01	2·80	
9	2·10	2·94	
10	2·18	3·08	
11	2·27	3·22	
12	2·35	3·34	
13	2·43	3·46	
14	2·51		

TABLE 2

Concentration of sodium sulphide solution diffusing from the top – 0·1 M

Number of rings	Concentration of cadmium sulphate in 6% gelatin gel				
	0·1 M	0·02 M	·01 M	·0066 M	0·005 M
	0 cms.	0 cms.	0 cms.	0 cms.	0 cms.
1	0·92	1·51	1·60	1·62	2·21
2	1·11	1·59	1·68	1·80	2·62
3	13·3	1·68	1·76	1·98	3·04
4		1·78	1·85	2·17	3·47
5		1·90	1·97	2·36	3·92
6		2·04	2·15	2·56	4·83
7		2·18	2·33	2·76	
8		2·34	2·53	2·97	
9		2·56	2·75	3·19	
10		2·88	3·05	3·41	
11		3·29	3·37	3·73	
12		3·83	3·82	4·07	
13				4·67	

A persual of table 1 shows that the distances between successive rings decrease as the distance of the ring from the top of the gel increases and table 2 shows that the distances between successive rings go on increasing. 'Revert' type of rings as given in table 1, are obtained because the sol of cadmium sulphide is coagulable by sodium sulphide and stabilized by cadmium ions.

In agar agar medium the Liesegang rings of cadmium sulphide are observed when cadmium sulphate solution is allowed to diffuse in the agar agar gel containing sodium sulphide. The results are presented in the following table :

TABLE 3

Concentration of cadmium sulphate solution diffusing from the top – 0·1 M

Number of rings	Concentration of sodium sulphide in 10% agar agar gel				
	0·1 M	0·04 M	0·02 M	0·01 M	0·005 M
	0 cms.	0 cms.	0 cms.	0 cms.	0 cms.
1	0·74	0·90	1·72	2·04	2·45
2	0·94	1·28	2·48	2·76	3·51
3	1·15	1·71	3·27	3·84	
4	1·36	2·34			
5	1·58	3·13			
6	1·80	3·95			
7	2·08				
8	2·38				
9	2·78				
10	3·20				
11	3·80				

A perusal of table 3 shows that the distances between successive rings go on increasing as the distance of the ring from the top of the gel increases *i.e.* 'Direct' type of rings are formed. Better rings are obtained when the concentration of sodium sulphide in agar agar gel is 0·1 M. Diffused rings of cadmium sulphide are observed when sodium sulphide solution is allowed to diffuse from the top in the agar agar gel containing cadmium sulphate.

Liesegang rings of cadmium sulphide are also obtained in the starch medium when cadmium sulphate solution is allowed to diffuse in 6% starch gel containing sodium sulphide. Such results are presented in the following tables :

TABLE 4

Concentration of cadmium sulphate solution diffusing from the top – 0·1 M

Number of rings	Concentration of sodium sulphide in 6% starch gel		
	0·02 M	0·01 M	0·005 M
		0 cms.	
1	No rings	1·23	No rings
2		1·53	
3		1·83	
4		2·16	
5		2·48	

TABLE 5

Concentration of Cadmium sulphate solution diffusing from the top – 0·04 M

Number of rings	Concentration of sodium sulphide in 6% starch gel		
	0·02 M	0 01 M	0·005 M
		0 cms.	
1	No rings	1·04	No rings
2		1·34	
3		1·64	
4		1·96	

Rings are formed when the concentration of sodium sulphide in the starch gel is 0·01 M. Periodic precipitation of cadmium sulphide is not observed when sodium sulphide solution is allowed to diffuse in starch gel containing cadmium sulphate. In the presence of small quantities of acid in the starch gel along with cadmium sulphate well defined rings of cadmium sulphide are observed on the diffusion of sodium sulphide solution from the top. The results are presented in the following table:

TABLE 6

Concentration of sodium sulphide solution diffusing from the top – 0 02 M

Concentration of hydrochloric acid in starch gel – 0·005 M

Number of rings	Concentration of cadmium sulphate in 6% starch gel		
	0·02 M	0·01 M	0·005 M
	0 cms.	0 cms.	0 cms.
1	0·24	0·67	0·88
2	0·32	0·78	1·04
3	0·38	0 68	1·18
4	0·44	0·97	1·32
5	0·50	1·06	1 46
6	0·55	1·15	1·58
7	0·59	1·24	1·70
8	0·63	1·32	1·80
9		1 40	
10		1·48	
11		1·56	
12	1·63	1·63	

A perusal of the above table shows that the distances between the successive rings go on decreasing as the distance of the rings from the top of the gel increases *i.e.* 'Revert' type of rings are obtained. It is so because the sol of cadmium sulphide in starch medium is coagulable by cadmium sulphate and hydrochloric acid and stabilized by sodium sulphide.

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Dusty Viscous Fluid Flow between Rotating Coaxial Cylinders

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Abstract

In the present paper, an analytical solution of the laminar flow of an unsteady, incompressible, viscous fluid with uniform distribution of dust particles through two rotating coaxial cylinders under the influence of an axial pressure gradient has been obtained. It has been found that the velocity of the dust particles is more than that of the fluid particle. In the case of very fine dust particles, the velocity of the dust particle is the same as that of the fluid particle. When the masses of the dust particles tend to zero, the dusty fluid becomes ordinary viscous fluid.

1. Introduction

Saffman[6] has derived the governing equations of the flow of a dusty gas in which the dust is given in terms of a number density of small particles with very small volume concentration but appreciable mass concentration. In the same paper, he has discussed the stability of plane parallel flows to small disturbances. Michael[2] has discussed the Kelvin-Helmholtz instability of unidirectional flows of fluid particle mixtures with low volume densities of particles. Michael and Miller[3] have obtained the solutions for two problems of viscous laminar flows of such mixtures using the formulation of Saffman. The motion, induced in the gas having uniform distribution of dust, is considered in the two cases when the plane moves parallel to itself (*i*) in simple harmonic motion, and (*ii*) impulsively from rest with uniform velocity. The laminar flow of an unsteady viscous fluid with uniform distribution of dust particles through a circular cylinder under the influence of exponential pressure gradient has been investigated by Rao[5]. Miller[4] has discussed the motion and number density of particles initially at rest, under gravity in an incompressible, viscous fluid round a vertical solid cylinder in oscillatory rotation.

In the present paper, the laminar flow of an unsteady, incompressible viscous fluid with uniform distribution of dust particles through two rotating coaxial cylinders under the influence of an axial pressure gradient has been investigated. It has been assumed that the duty gas has a large number density of very small particles and the bulk concentration of the particles is so small that it can be neglected. The density of the dust material is taken to be large compared to the gas density. The particles of the dust are so small that the Stokes law of resistance between the particles and the gas holds good. The flow is assumed to be fully developed and axi-symmetric. Analytical expressions for velocities of the dust and fluid particles have been obtained.

2. Formulation of the problem

The equations of motion of a dusty, viscous, unsteady, and incompressible fluid as given by Saffman[6] are :

$$\frac{\partial \vec{u}}{\partial t} + (\vec{u}.\nabla)\vec{u} = -\frac{1}{\rho}\ \text{grad}\, p + \nu \nabla^2 \vec{u} + \frac{KS}{\rho}(\vec{v} - \vec{u}) \tag{1}$$

$$\text{div}\ \vec{u} = 0 \tag{2}$$

$$m\left[\frac{\partial \vec{u}}{\partial t} + (\vec{v}\,.\,\nabla)\vec{v}\right] = K(\vec{u} - \vec{v}) \tag{3}$$

$$\frac{\partial S}{\partial t} + \text{div}\ S\vec{v} = 0 \tag{4}$$

where $\vec{u}$, $\vec{v}$ are the local velocity vectors of fluid and dust particles respectively, ρ is the density, p is the static fluid pressure, ν is the kinmetic viscosity, K is the Stokes resistance coefficient (for spherical particles of radius a, it is $6\pi\,\mu a$), μ is the fluid viscosity, S is the number density of a dust particle, m is the mass of a dust particle.

Let us consider the unsteady flow of an incompressible, viscous, dusty fluid between two rotating coaxial cylinders of radii a and b under the influence of an axial pressure gradient. Let us assume that at $t = 0$ the two cylinders rotate in the same direction with constant angular velocities ω_1 and ω_2 respectively. Let us define the cylindrical coordinate (r, θ, z) with origin at a convenient point on the axis of the cylinder. Under these circumstances, the velocity distributions of fluid and dust particles can be expressed as[1] :

$$u_r = 0,\ u_\theta = u_\theta(r, t),\ u_z = u_z(r, t) \tag{5}$$

$$v_r = 0,\ v_\theta, = v_\theta(r, t),\ v_z = v_z(r, t) \tag{6}$$

$$S = S_0 = \text{constant}$$

where (u_r, u_θ, u_z) and $v_r, v_\theta, v_z)$ are the velocity components of the fluid and dust particles respectively. We introduce the dimensionless variables as follows : Let

$$\bar{u}_\theta = \frac{u_\theta}{\omega_2 b},\ \bar{u}_z = \frac{u_z}{\omega_2 b},\ \bar{v}_\theta = \frac{v_\theta}{\omega_2 b},\ \bar{v}_z = \frac{v_z}{\omega_2 b},$$

$$R = \frac{r}{b},\ \bar{p} = \frac{1}{2}\frac{p}{\rho\,\omega_2^2 b^2},\ \bar{t} = \frac{t}{T},\ \bar{y} = \frac{y}{T} = \frac{m}{KT}$$

where T and y are characteristic time and relaxation time respectively.

Using equations (5–7), the equations (1) and (3) can be expressed in non-dimensional form as :

$$\frac{\partial \bar{p}}{\partial R} = \frac{1}{2}\frac{\bar{\mu}_\theta^2}{R} \tag{8}$$

$$\frac{\partial \bar{u}_\theta}{\partial \bar{t}} = \lambda_1^2 \left[\frac{\partial^2 \bar{u}_\theta}{\partial R^2} + \frac{1}{R} \frac{\partial \bar{u}_\theta}{\partial R} - \frac{\bar{u}_\theta}{R^2} \right] + \frac{l}{y} (\bar{v}_\theta - \bar{u}_\theta) \tag{9}$$

$$\frac{\partial \bar{v}_\theta}{\partial \bar{t}} = \frac{1}{y} (\bar{u}_\theta - \bar{v}_\theta) \tag{10}$$

$$\frac{\partial \bar{v}_z}{\partial \bar{t}} = - \alpha_1 \frac{\partial \bar{p}}{\partial \bar{z}} + \lambda_1^2 \left(\frac{\partial^2 \bar{u}_z}{\partial R^2} + \frac{1}{R} \frac{\partial \bar{u}_z}{\partial R} \right) + \frac{l}{y} (\bar{v}_z - \bar{u}_z) \tag{11}$$

$$\frac{\partial \bar{v}_z}{\partial \bar{t}} = \frac{1}{y} (\bar{u}_z - \bar{v}_z) \tag{12}$$

where $l = \frac{mS_0}{\rho}$ is the mass concentration of the dust particles, $\lambda_1^2 = \nu T/b^2$ and $\alpha_1 = 2\omega_2 T$ are constants.

3. Solution of the problem

The governing equations are partial differential equations. In order to reduce them to ordinary differential equation, let us assume that :

$$- \frac{\partial \bar{p}}{\partial \bar{z}} = \beta e^{-\lambda^2 \bar{t}} \tag{13}$$

$$\bar{\omega}_i = \omega_i e^{-\lambda^2 \bar{t}} \qquad (i = 1, 2)$$

$$\bar{u}_\theta = f(R) \, e^{-\lambda^2 \bar{t}}$$

$$\bar{v}_z = F(R) \, e^{-\lambda^2 \bar{t}}$$

$$\bar{v}_\theta = g(R) \, e^{-\lambda^2 \bar{t}}$$

$$\bar{v}_z = G(R) e^{-\lambda^2 \bar{t}}$$

where β and λ are real contants f, F, g, G are functions of R only, and $\bar{\omega}_i$ is the angular velocity of cylinders for $t > 0$.

Substituting for $\bar{u}_\theta$ and $\bar{v}_\theta$ from equation (13) in equations (9) and (10), we have :

$$\frac{d^2 f}{dR^2} + \frac{1}{R} \frac{df}{dR} + \left(n^2 - \frac{1}{R^2} \right) f = 0 \tag{14}$$

$$g = \frac{f}{1 - y \lambda^2} \tag{15}$$

where $n = \frac{\lambda'}{\lambda_1^2} \left[1 + \frac{l}{1 - y \lambda^2} \right]$ is constant.

The boundary conditions are :

$$R = a/b = \xi, f = N = \frac{a\,\omega_1}{b\,\omega_2}, \qquad (16)$$
$$R = 1\ ,\ f = 1.$$

The solution of equation (14) with boundary conditions given by (16) is :

$$f(R) = A\,J_1\,(nR) + B\,Y_1\,(nR) \qquad (17)$$

where

$$A = \frac{N\,Y_1(n) - Y_1(n\xi)}{J_1(n\xi)\,Y_1(n) - J_1(n)\,Y_1(n\xi)}$$

$$B = \frac{J_1(n\xi) - N\,J_1(n)}{J_1(n\xi)\,Y_1(n) - J_1(n)\,Y_1(n\xi)}$$

J_1 and Y_1 are the first and second kind of Bessel functions of order one. Hence, if we know $f(R)$, $g(R)$ can be obtained from equation (15).

The tangential velocity components of the fluid and dust particles are given by :

$$\bar{u}_\theta\,(R, \bar{t} = [A\,J_1(nR) + B\,Y_1(nR)]\,e^{-\lambda^2\bar{t}} \qquad (18)$$

and

$$v_\theta\,(R, \bar{t}) = \frac{1}{(1 - \bar{y}\,\lambda^2)}\,[A\,J_1(nR) + B\,Y_1(nR)]\,.e^{-\lambda^2\bar{t}} \qquad (19)$$

Similarly. substituting for $\bar{u}_z$ and $\bar{v}_z$ from equation (13) in equations (11) and (12), we get :

$$\frac{d^2F}{dR^2} + \frac{1}{R}\frac{dF}{dR} + n^2\,(F + \Omega) = 0 \qquad (20)$$

and

$$G = \frac{F}{1 - \bar{y}\,\lambda^2} \qquad (21)$$

where

$$\Omega^2 = \frac{a}{\lambda^2}\left[\frac{(1 - \bar{y}\,\lambda^2)}{1 - \bar{y}\,\lambda^2 + l}\right]$$

and $a = \alpha_1\,\beta$, Ω, and a are constant quantities.

$$R = \xi,\quad F = 0,$$
$$R = 1,\quad F = 0, \qquad (22)$$

The solution of equation (20) with boundary conditions given by (22) is :

$$F(R) = C\,J_0\,(nR) + D\,Y_0(nR) - \Omega \qquad (23)$$

where

$$C = \frac{\Omega[Y_0(\xi n) - Y_0(n)]}{J_0(n)\,Y_0(\xi n) - J_0(\xi n)\,Y_0(n)}$$

$$D = \frac{\Omega[J_0(n) - J_0(\xi n)]}{J_0(n)\,Y_0(\xi n) - J_0(\xi n)\,Y_0(n)}$$

J_0 and Y_0 are the first and second kind of Bessel functions of order zero. Knowing $F(R)$, $G(R)$ can be obtained from equation (21). Hence, the axial velocities of the fluid and dust particles are given by :

$$\bar{u}_z(R, \bar{t}) = [C J_0(nR) + D Y_0(nR) -] \Omega e^{-\lambda^2 \bar{t}} \tag{24}$$

and

$$\bar{v}_z(R, \bar{t}) = \frac{1}{1 - \bar{y}\lambda^2} [C J_0(nR) - D Y_0(nR) - \Omega] e^{-\lambda^2 \bar{t}} \tag{25}$$

When $|n|$ is large, we take $n^2 = -n'^2$, then the solution of equation (14) becomes :

$$f(R) = A I_1(n'R) + B K_1(n'R) \tag{26}$$

where

$$A = \frac{N K_1(n') - K_1(n'\xi)}{K_1(n') I_1(n'\xi) - I_1(n') K_1(n'\xi)}$$

$$B = \frac{I_1(n'\xi) - N I_1(n')}{I_1(n'\xi) K_1(n') - I_1(n') K_1(n'\xi)}$$

I_1 and K_1 are modified Bessel functions of 1st and 2nd kind of order one. Since $|n|$ is large, taking the asymptotic values of the Bessel functions, equations (18) and (19) can be expressed as

Hence

$$\bar{u}_\theta(R, \bar{t}) = \left[A \frac{e^{n'R}}{(2\pi nR)^{\frac{1}{2}}} + \left(\frac{\pi}{2n'R}\right)^{\frac{1}{2}} e^{-n'R} \right] e^{-\lambda^2 \bar{t}} \tag{27}$$

$$\bar{v}_\theta(R, \bar{t}) = \frac{1}{1-\bar{y}\lambda^2} \left[A \frac{e^{n'R}}{(2\pi n'R)^{\frac{1}{2}}} + B \left(\frac{\pi}{2n'R}\right)^{\frac{1}{2}} e^{-nR} \right] e^{-\lambda^2 \bar{t}} \tag{28}$$

where

$$A = (2\pi n')^{\frac{1}{2}} \left[\frac{-N(\xi)^{\frac{1}{2}} e^{-n'} + e^{-n'\xi}}{e^{n'(1-\xi)} - e^{-n'(1-\xi)}} \right]$$

$$B = \left(\frac{2n'}{\pi}\right)^{\frac{1}{2}} \left[\frac{N(\xi)^{\frac{1}{2}} e^{n'} - e^{-n'\xi}}{e^{n'(1-\xi)} - e^{-n'(1-\xi)}} \right]$$

Similarly, for large $|n|$, the equations (24) and (25) can be expressed as :

$$\bar{u}_z(R, \bar{t}) = \left[C \frac{e^{n'R}}{(2\pi n'R)^{\frac{1}{2}}} + D \left(\frac{\pi}{2n'R}\right)^{\frac{1}{2}} e^{-n'R} - \Omega \right] e^{-\lambda^2 \bar{t}} \tag{29}$$

$$\bar{v}_z(R, \bar{t}) = \frac{1}{1-\bar{y}\lambda^2} \left[C \frac{e^{n'R}}{(2\pi n'R)^{\frac{1}{2}}} + D \left(\frac{\pi}{2n'R}\right)^{\frac{1}{2}} e^{-n'R} - \Omega \right] e^{-\lambda^2 \bar{t}} \tag{30}$$

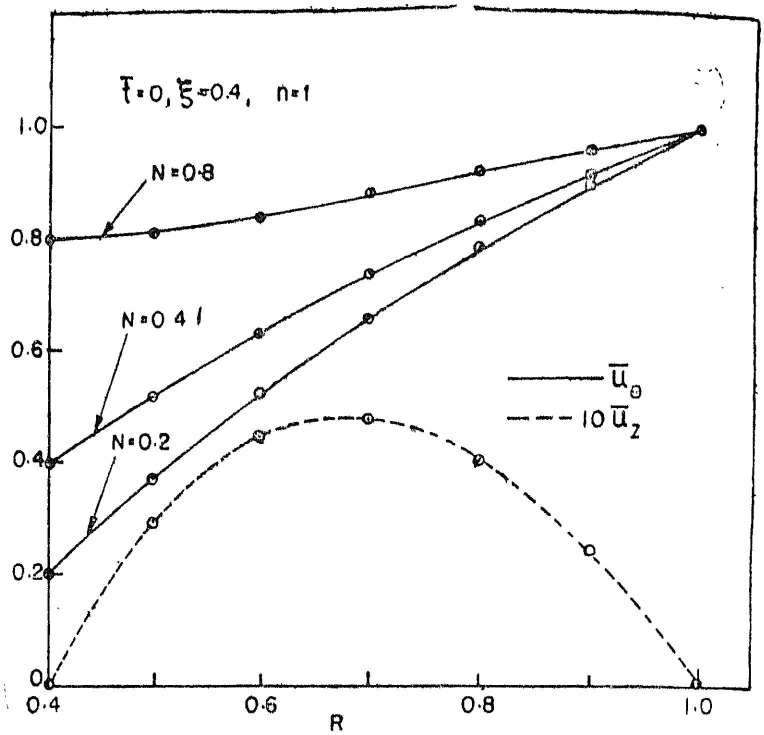

FIG. 1. VELOCITY DISTRIBUTIONS

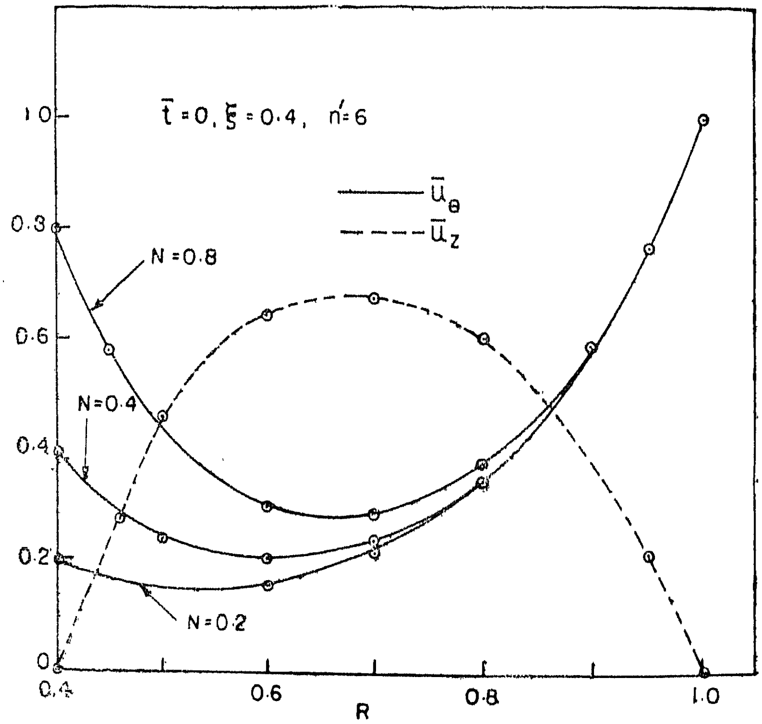

FIG 2. VELOCITY DISTRIBUTIONS

where

$$C = \frac{\Omega(2\pi n')^{\frac{1}{2}} [e^{-n'\xi} - (\xi)^{\frac{1}{2}} e^{-n'}]}{[e^{n'(1-\xi)} - e^{-n'(1-\xi)}]}$$

$$D = \frac{\Omega\left(\frac{2n'}{\pi}\right)^{\frac{1}{2}} \left[(\xi)^{\frac{1}{2}} e^{n'} - e^{n'\xi} \right]}{[e^{n'(1-\xi)} - e^{-n'(1-\xi)}]}$$

4. Discussions of numerical results

The tangential and axial velocity components of the fluid are calculated by taking $N = 0{\cdot}8$, $0{\cdot}4$ and $0{\cdot}2$, $\xi = 0{\cdot}4$, $n = 1$, $n' = 6$ and $\bar{t} = 0$. They are given in Figs. 1 and 2. The behaviour of the tangential and axial velocities of the dust is the same as those of the fluid except that they are greater than those of the fluid by a constant factor.

It can be seen that the tangential velocities of the fluid and dust particles decrease in the region of the inner cylinder if the ratio of the angular velocities of outer and inner cylinders increases both for small and large n The axial velocity components of the fluid and dust particles are independent of the angular velocities of the cylinders. For small n, $\bar{u}_\theta$, and $\bar{v}_\theta$ continuously increase from the inner cylinder to the outer cylinder, but for large n, they first decrease near the inner cylinder and then they increase. The axial velocity components $\bar{u}_z$, and $\bar{v}_z$ increase as n increases except on inner and outer cylinder. The velocity components tend to zero as $\bar{t}$ tends to ∞.

5. Conclusions

(*i*) The tangential and axial velocities of the dust particle are greater than those of the fluid particle but they become same as the relaxation time tends to zero *i e.* when the dust particles become very fine.

(*ii*) If the masses of the dust particles are small, their influence on the fluid flow is reduced and as the mass of the dust particle tends to zero, the fluid flow tends to ordinary viscous laminar flow.

(*iii*) The velocity components of the fluid and the dust particles tend to zero as the time $\bar{t}$ tends to ∞.

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Adsorption of Dichromate Ions by Hydrous Cadmium Oxide

By

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Abstract

The adsorp.ion of dichromate ions by cadmium hydrous oxide samples has been studied at different temperatures, and the heats of adsorption values have been calculuted. It is observed that in general the adsorption increases up to 40°C, but afterwards it slightly falls off in samples A and C. The heats of adsorption values are negative and in the lower range of temperature 35° – 40° of the order of 10 – 30 K Cals/mole, but in the higher range the value are low or even positive. Freundlich's equation is found applicable in all samples, but Langmuir's equation does not hold good. In some cases (sample B) the adsorption isotherms are also S-shaped. The order of adsorption for different samples is $A < B \geqslant C$. Thus the adsorption of $Cr_2O_7^{--}$ by cadmium hydrous oxide appears to be a case of chemisorption preceded by physical adsorption, which may also become multilayered in some cases.

Introduction

Hydrous Oxides are well known to be very good adsorbents for ions and dyes. Ghosh[1] and coworkers have reported that the character of an hydrous oxide depends upon the pH of the precipitating medium, temperature and its age and have studied the adsorption of various ions and dyes from this point of view. The present paper deals with a systematic study of the adsorption of dichromate ions by three samples of cadmium hydrous oxide, precipitated under different conditions.

Experimental

Three samples A, B and C of hydrous cadmium oxides were prepared by precipitating them with 20% deficient, equivalent and 20% excess of sodium hydroxide from a solution of cadmium sulphate. They were thoroughly washed free of ions and their homogeneous suspensions were stored in jena glass bottles with air tight stoppers. The pH values of the three samples were measured and found to be 8·4, 9·25 and 9 3 respectively. The cadmium contents of the three samples were estimated in 5 ml. portions and found as (A) : $208{\cdot}5 \times 10^{-6}$, (B): $205{\cdot}0 \times 10^{-6}$ and (C) : $230{\cdot}0 \times 10^{-6}$ gram/moles of CdO respectively. In order to avoid the effect of ageing, all the adsorption studies described in this paper have been made on one month aged samples.

Five ml. of the above suspensions were taken in each of a set of boiling tubes. In another set of boiling tubes different volume (5, 10, 15, 20, 25 and 30 ml.) of M/120 potassium discromate solution were taken and raised to 35 ml. in each case. Then the suspension and potassium dichromate solutions were suspended into a thermostat to attain the temperature (30° ± ·1°C) of the thermostat. After about half an hour the potassium dichromate solutions were

poured into the suspensions and mixed well. They were again kept in the same thermostat at the same constant temperature (30° ± ·1°C) for a definite interval of time. They were then taken out and the supernatant liquids were centrifuged. In the centrifugate $Cr_2O_7^{--}$ was estimated idometrically. Similarly other series of experiments were performed with all the three samples at various intervals of time (15 mins., 30 mins., 1 hour, 1½ hours, 2 hours, 3 hours and overnight).

From the results obtained, the end concentration, the amount of $Cr_2O_7^{--}$ adsorbed and x/m were calculated. The results are graphically represented in Figs. 1-3, where x/m ratios are plotted against time, which show that in general the majority of the adsorption occurs within a few minutes of contact of the hydrous cadmium oxide precipitates and potassium dichromate.

Effect of Temperature

The effect of temperature on the adsorption of $Cr_2O_7^{--}$ was investigated by studying its adsorption at three different temperatures 35°, 40° and 45°C. The time of contact of the suspensions with dichromate solution was kept four hours. From the results the rasidual concentrations, and x/m ratios were calculated. The results are graphically represented in Figs. 4-6.

Further, to have a comparative idea of the adsorptive capacities of the three samples, x/m ratios (at 45°C alone) have been plotted against residual concentration for all three samples A, B and C together in Fig. 7.

In Figs. 8-10 the applicability of Freundlich's adsorption equation has been tested by plotting x/m ratios against log C for all the three samples A, B and C. From the curve S, it is clear that in general Freundlich's equation holds good in all three cases. Attempts were also made to test the applicability of Langmuir's equation, but it was found that it is not applicable in these cases.

Heat of Adsorption

The heat of adsorption, Q is given by the equation[7]

$$Q = \frac{R\,T_1\,T_2}{(T_1 - T_2)} \times 2{\cdot}303 \log C_1/C_2$$

when C_1 and C_2 are the residual concentrations of the ions adsorbed at the respective temperatures T_1 and T_2, for the same amount of adsorption. The values of residual concentrations C_1, C_2 and C_3 for respective temperatures have been extrapolated from the adsorption isotherms in Figs. 4-6. From these the values of Q for different ranges of adsorption and temperature were calculated. The results are given in the following tables I-III.

TABLE I
Sample 'A'

	x/m	(45-40)°C		(40-35)°C		(45-35)°C	
		log C_1-C_2	Q in c l	log C_2-C_3	Q in cal	log C_1-C_3	Q in cal
1	·20	·0284	2040	-·1980	-17471	-·2096	-9496
2	·18	·0322	2339	-·2725	-24045	-·2413	-10817
3	·16	·0294	2127	-·2972	-26224	-·2678	-11985
4	·14	·0341	2467	-·3220	-28413	-·2885	-12933
5	·12	·0307	2231	-·3557	-31386	-·3250	-14569
6	·10	·0248	1794	-·3661	-32304	-·3413	-15300

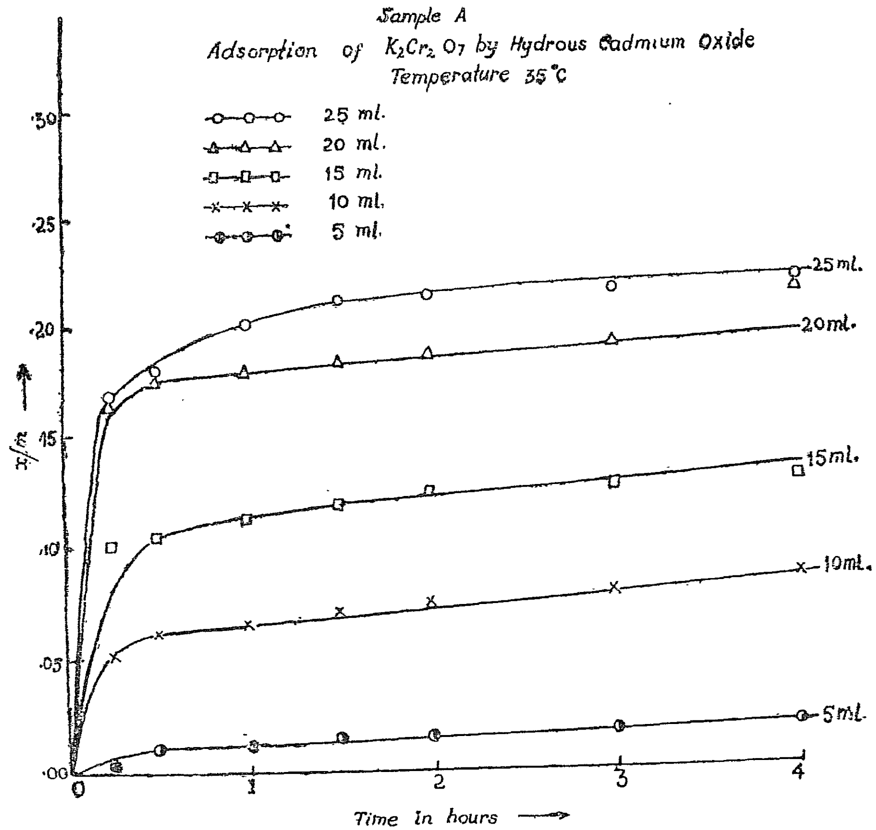
Sample A
Adsorption of $K_2Cr_2O_7$ by Hydrous Cadmium Oxide
Temperature 35°C
25 ml.
20 ml.
15 ml.
10 ml.
5 ml.
·30
·25
·20
·15
·10
·05
·00
x/m
0
1
2
3
4
25ml.
20ml.
15ml.
10ml.
5ml.
Time in hours

FIG. 1

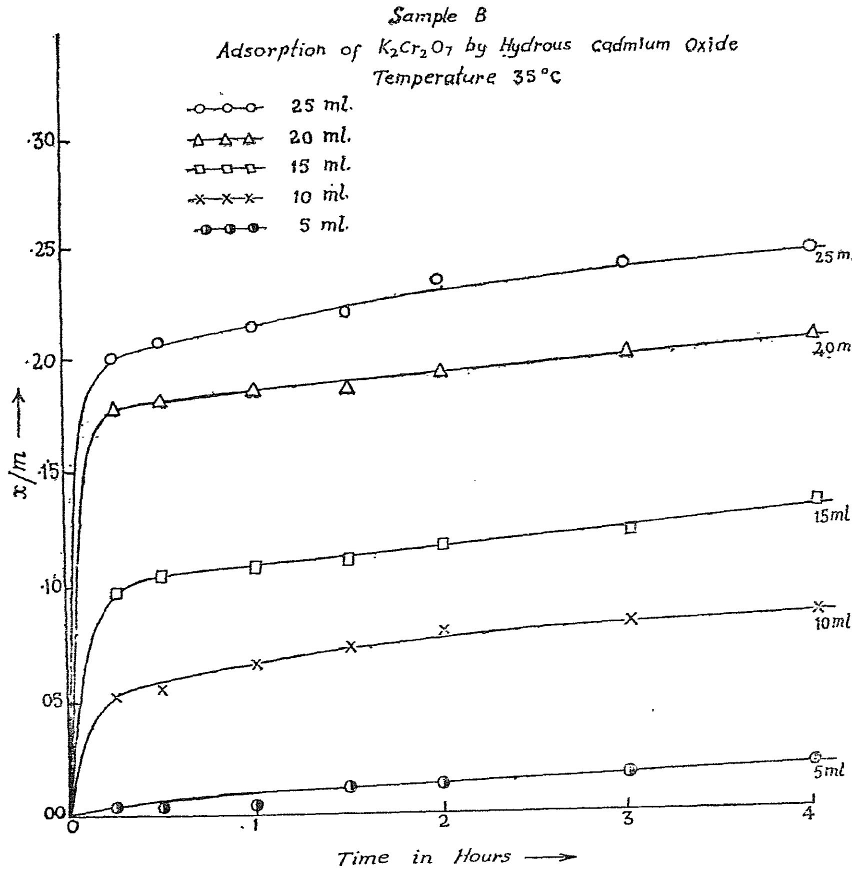
Sample B
Adsorption of $K_2Cr_2O_7$ by Hydrous Cadmium Oxide
Temperature 35°C
25 ml.
20 ml.
15 ml.
10 ml.
5 ml.
·30
·25
·20
·15
·10
·05
·00
x/m
0
1
2
3
4
15ml
10ml
5ml
Time in Hours

FIG. 2

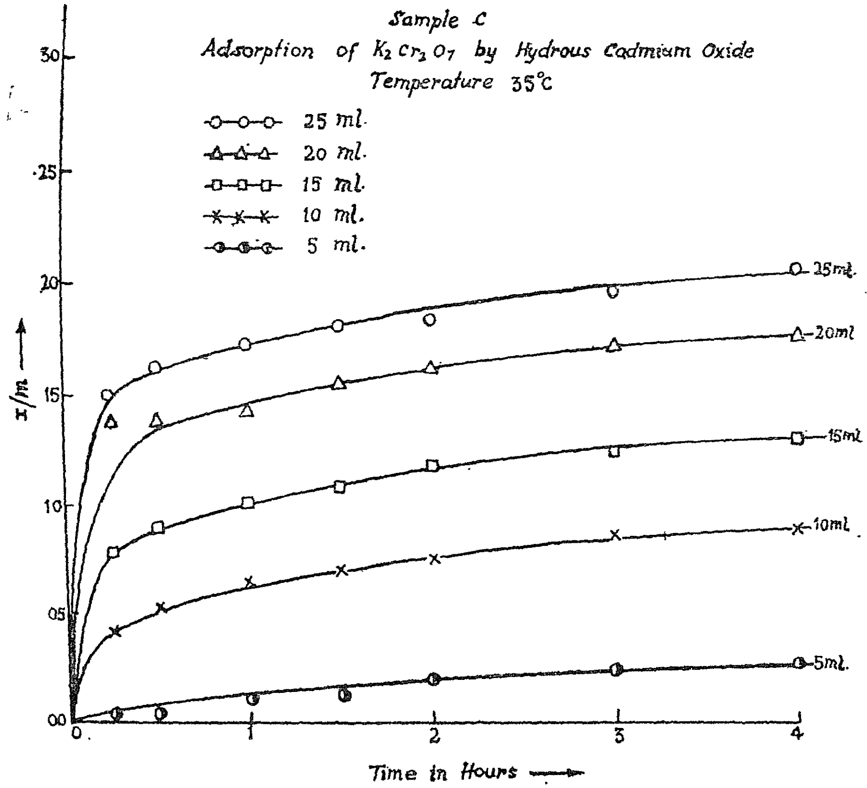
Sample C
Adsorption of $K_2Cr_2O_7$ by Hydrous Cadmium Oxide
Temperature 35°C
25 ml.
20 ml.
15 ml.
10 ml.
5 ml.
x/m
Time in Hours

FIG. 3

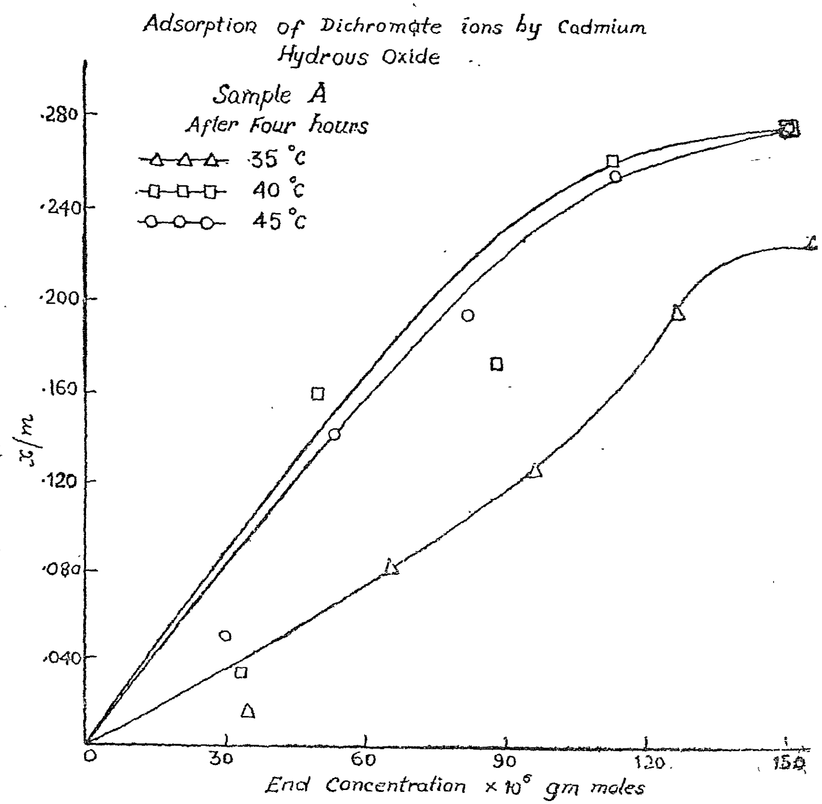
Adsorption of Dichromate ions by Cadmium Hydrous Oxide
Sample A
After Four hours
35 °C
40 °C
45 °C
x/m
End Concentration × 10^6 gm moles

FIG. 4

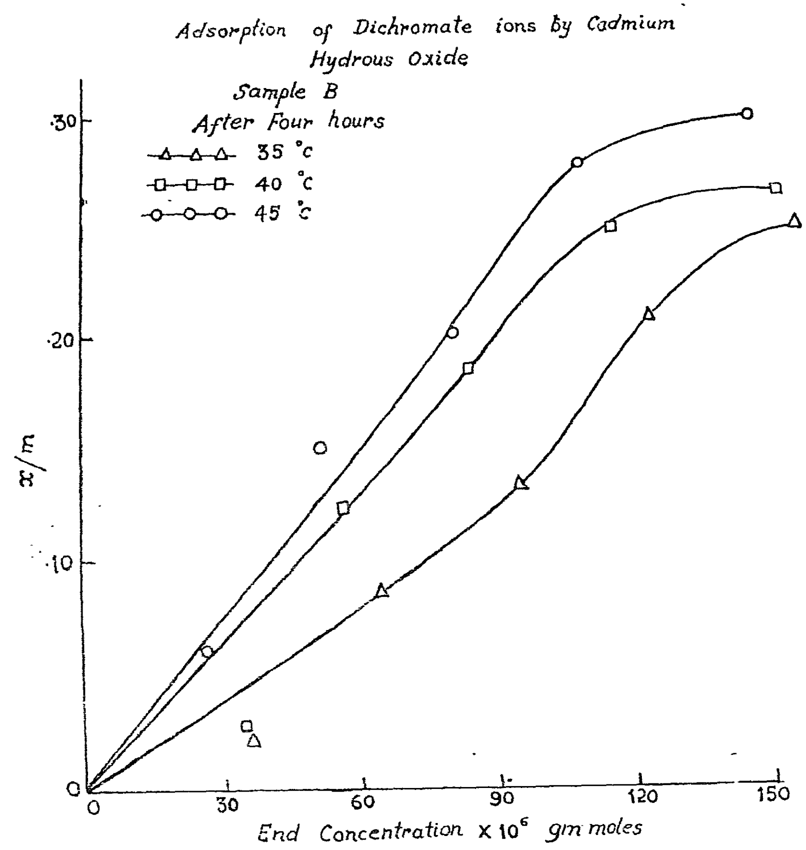
Adsorption of Dichromate ions by Cadmium
Hydrous Oxide
Sample B
After Four hours
35 °c
40 °c
45 °c
x/m
·30
·20
·10
0
0
30
60
90
120
150
End Concentration x 10⁶ gm moles

FIG. 5

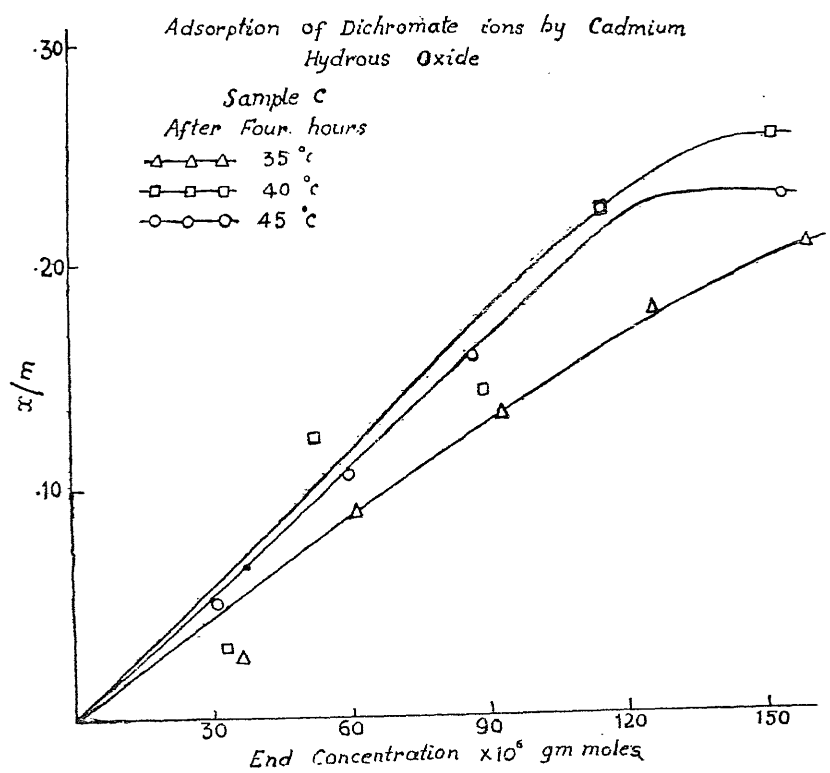
Adsorption of Dichromate ions by Cadmium
Hydrous Oxide
Sample C
After Four hours
35 °c
40 °c
45 °c
x/m
·30
·20
·10
30
60
90
120
150
End Concentration x10⁶ gm moles

FIG. 6

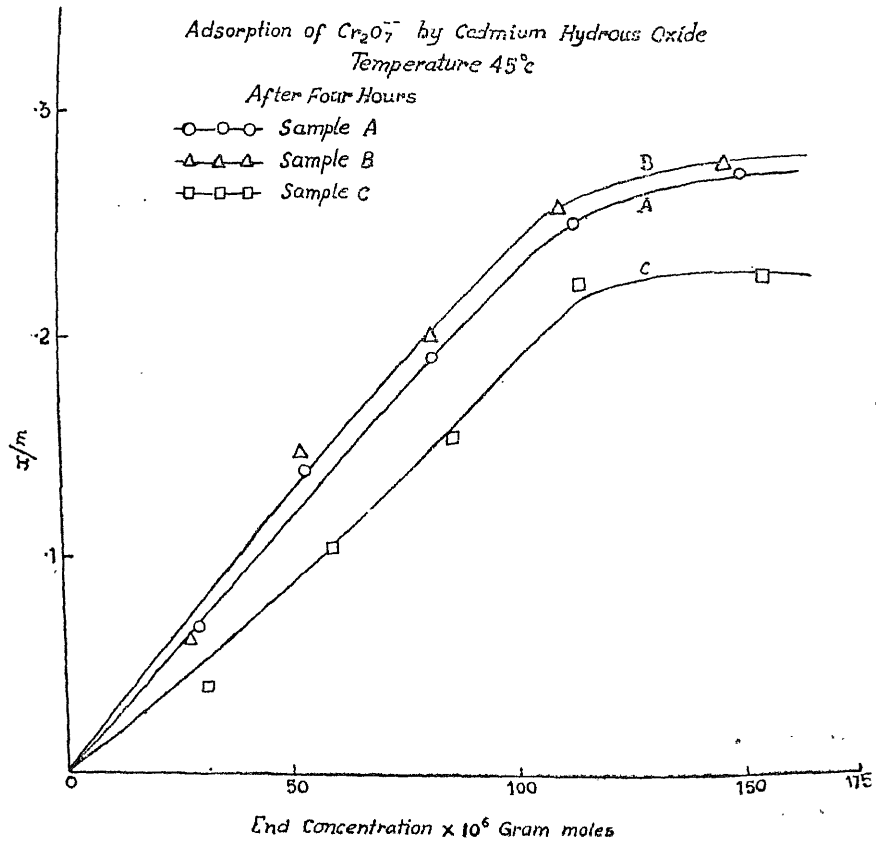
Adsorption of $Cr_2O_7^{--}$ by Cadmium Hydrous Oxide
Temperature 45°c
After Four Hours
Sample A
Sample B
Sample C
B
A
C
x/m
·3
·2
·1
0
50
100
150
175
End Concentration × 10^6 Gram moles

FIG. 7

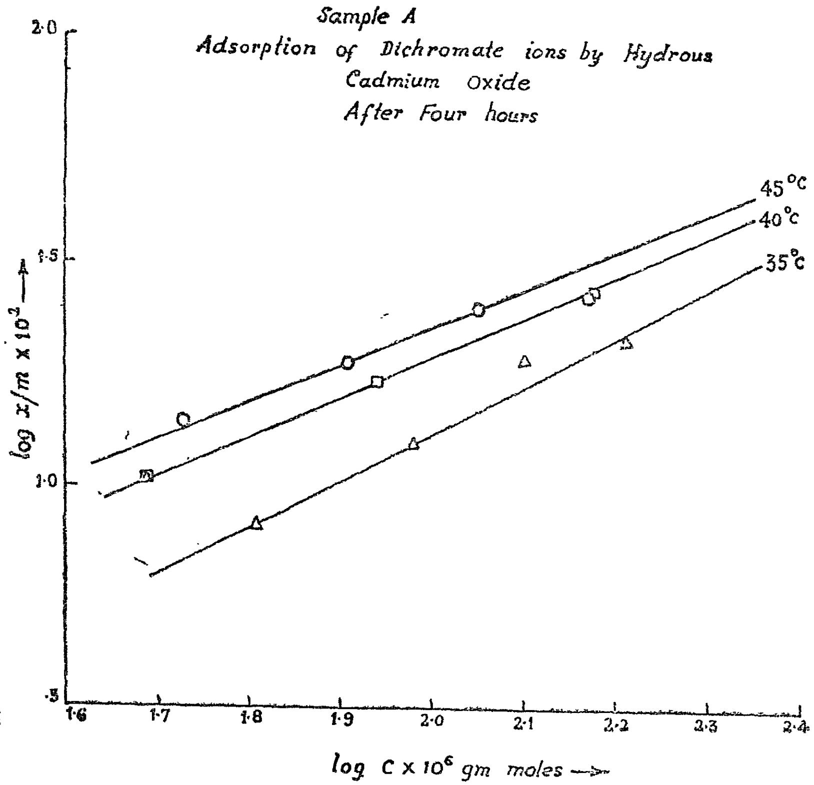
Sample A
Adsorption of Dichromate ions by Hydrous
Cadmium Oxide
After Four hours
45°C
40°C
35°C
log x/m × 10^2
2·0
1·5
1·0
·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
log C × 10^6 gm moles

FIG 8

Sample B

Adsorption of Dichromate ions by Hydrous Cadmium Oxide

After Four hours

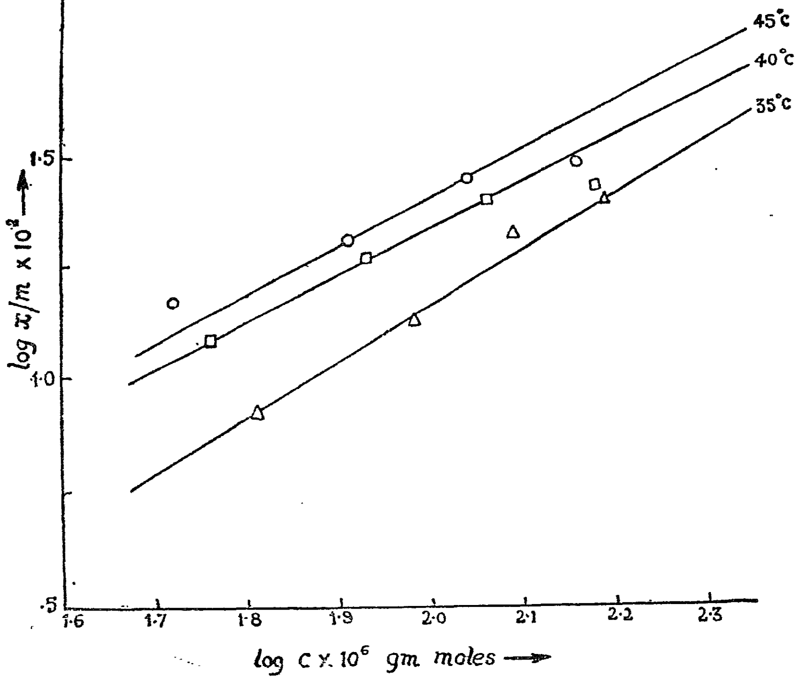

FIG. 9

Sample C

Adsorption of dichromate ions by Hydrous Cadmium Oxide

After Four hours

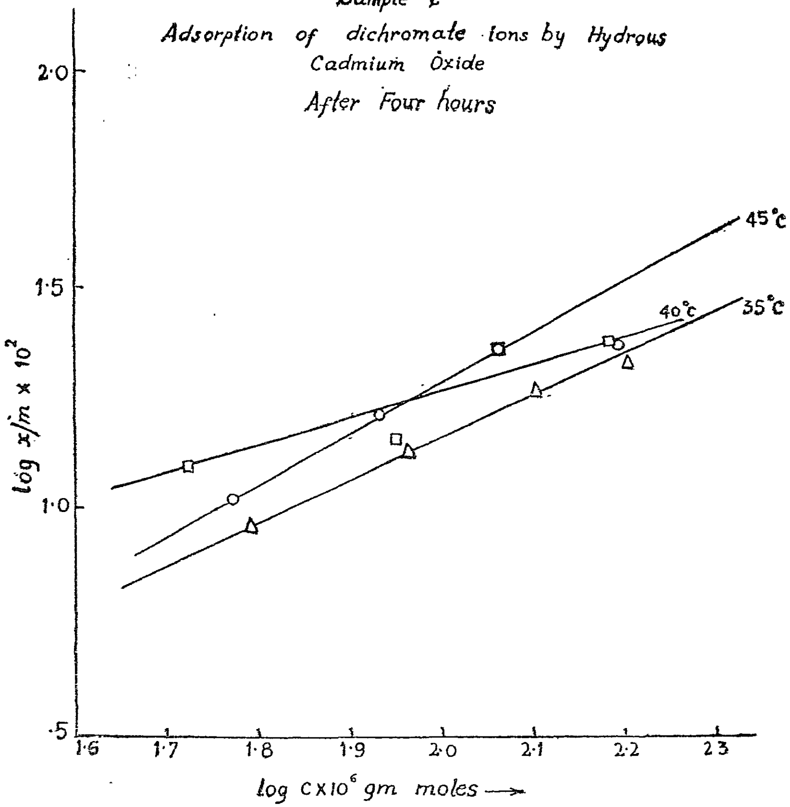

FIG. 10

TABLE II

Sample 'B'

	x/m	(45–40)°C		(40–35)°C		(45-35)°C	
		log C_1/C_2	Q in cal	log C_2/C_3	Q in cal	log C_1/C_3	Q in cal
1	·20	–·0505	–3654	–·1238	–10934	–·1743	–7813
2	·18	–·0551	–3987	–·11326	–11700	–·1877	–8414
3	·16	–·0556	–4023	–·1583	–13968	–·2139	–9589
4	·14	–·0702	–5079	–·1739	–15344	–·2441	–10943
5	·12	–·0580	–4196	–·2012	–17753	–·2592	–11619
6	·10	–·0791	–5723	–·2055	–18115	–·2844	–12739

TABLE III

Sample 'C'

	x/m	(45–40)°C		(40–35)°C		(45-35)°C	
		log C_1/C_2	Q in cal	log C_2/C_3	Q in cal	log C_1/C_3	Q in cal
1	·20	·0248	1794	–·1675	–14780	–·1427	–6279
2	·18	·0230	1664	–·1468	–12943	–·1238	–5449
3	·16	·0260	1881	–·1043	–9301	–·1773	–7948
4	·14	·0290	2098	–·1390	–12344	–·1109	–4971
5	·12	·0271	1961	–·1319	–11267	–·1048	–4698
6	·10	·0244	1765	–·1228	–10735	–·0984	–4410

Discussion

In the Figs. 1–3 results are presented for the adsorption of $Cr_2O_7^{--}$ respectively on the three samples A, B and C of hydrous cadmium oxide with time. It is clear from the curves that major fraction of adsorption occurs within a few minutes of contact, after which the process becomes slow, equilibrium being attained in three to four hours. This indicates chemisorption, preceded by physical adsorption.

The results on the adsorption of $Cr_2O_7^{--}$ at three different temperature 35°, 40° and 45° are represented by the Figs. 4-6. From the curves, it is clear that in sample 'B' the adsorption increases with rising temperature, but in sample A and C the adsorption increases upto 40°C, but after that it slightly falls off with rising temperature. It is characteristics of chemical adsorption[2]. This is also confirmed by the fact that in these cases the adsorption increases rapidly at lower concentrations, but soon it reaches saturation value, and remains almost constant at that particular temperature. The curves for sample B and sample A (at 35° alone) are also some what S-shaped, being convex to concentration axis.

Tables 1-3 record, the heats of adsorption for the three samples of hydrous cadmium oxide for dichromate ions between different ranges of temperature. The results show that in sample B the values are throughout negative, although the values are much suppressed in the range of 40° - 45°C. In samples A and C the values are negative, when calculated for the range 35°–40° and 35°45°, but in the range of 40° – 45°C the values assume a positive value. It means that in general the adsorption of $Cr_2O_7^{--}$ is an endothermic process, but at higher temperatures in samples A and C, it becomes some what exothermic. Further between

40°-45° the values are low (-3600 to -6000 cals/moles for sample B, and approximately 2000 Cals/moles in samples A and C), whereas in the lower range of 35°-40° the heats of adsorption values are pretty high (from about 10,000-30,000 Cals/moles). This thus explains why the adsorption increases upto 40°C, but that it falls off with rising temperature in samples A and C, and in sample B the differences are slight between 40°-45°C.

Further, it is evident from these tables that in general the heat of adsorption decrease with the increase in the amount of dichromate ions adsorbed. Similar results have been reported by Hajela and Ghosh[3] in the adsorption of crystal violet by hydrous chromium and ferric oxides, by Taylor[4] and Langmuir in the case of oxygen on charocal, and by Bull[5] *et al* in the case of ethylene on tantalum. It may be due to the following two reasons:

(1) On a heterogeneous surface, the active spots are statistically distributed. At first the most active spots are covered, their less active spots being covered afterwards gradually, and hence the heat of adsorption decreases with the increase in the amount of adsorption.

(2) Another factor for the decreasing values of the heat of adsorption may be due to the repulsion of same type of charged ions which are already adsorbed by the hydrous oxide.

The curves in Figs. 8-10 show that in general the Freundlich's adsorption equation is applicable, but when attempts were made to test the applicability of Langmuir's equation, it was found not applicable.

Fig. 7 gives a comparative idea of the adsorptive capacities of the three samples A, B and C of hydrous cadmium oxide. It shows that in the adsorption of $Cr_2O_7^{--}$, the adsorption is least for sample C, the highest for sample B and for sample A it is slightly less than sample B. This different behaviour by different samples can be again explained by differences in the alkalinity of these samples. Because here the adsorption of a negative ion is involved, so it is the least in the case of most alkaline sample C, precipitated by excess of alkali. The larger adsorption by sample B as compared to sample A may be due to greater surface in sample B, as suggested earlier[6].

Thus the order of adsorption by these samples for $Cr_2O_7^{--}$ is $C < B \geqslant A$ whereas for Cu^{++} ions the order was $A > B \geqslant C$.

In the case of other amphoteric hydrous oxides as of chromium, iron, aluminium, bismuth etc. Ghosh[7] *et al* have reported the order to be $A < B < C$ in the case of cations, and $A > B > C$ in the case of anions. This different behaviour in the case of hydrous cadmium oxide samples can be explained by weak amphoteric nature of cadmium.

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An Extension of Bolzano—Weierstrass Theorem to the field of Ultra Real Numbers

By

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1. Introduction

The proof of Bolzano-Weierstrass theorem for the field of real numbers, R, is well known. This theorem has also been proved for R^n $(n \geqslant 1)$, the Euclidean space of n dimensions consisting of all ordered n-tuples $(x_1, x_2 \ldots x_n)$ of real numbers. After introducing a partial ordering in R^n $(n \geqslant 1)$ an interesting proof of this theorem has been given by Shukla[1]. Proceeding on similar lines we propose here to extend this theorem to the field of Ultra real numbers, *viz.* R^*. For the concept of ultrareal numbers the reader is referred to Robinson[2] as well as to Prasad[3]. Here we shall simply mention below those characteristics of R^* which we need in the proof of our theorem.

2. *Structure of R^*.*

The Ultra real number system R^* consists of all real sequences so that $R^* = \{f : f(n) \in R \text{ for all } n \in N\}$. Finite elements, infinite elements and infinitesimals exist in R^*. f is said to be a finite element in R^* if $|f(n)| \leqslant r$ for some positive $r \in R$ and all $n \in N$. Other elements are called Infinite elements. Constant sequences are called standard elements and others are called nonstandard elements. A standard element f identifies with a real number r iff $f(n) = r$ for all $n \in N$.

R^* is totally ordered and of any two ultrareal numbers f and g we say that $f \leqslant g$ iff $\{n : f(n) \leqslant g(n)\} \in U$, the ultrafilter on N which includes the complements of all finite subsets of N. Similar is the notion of the relation $\geqslant$, $<$, $=$ or $>$ in R^*.

3. *Concept of Supremum, Neighbourhood and Limiting Point.*

We now turn to the concept of boundedness in R^*. For a set A^* of ultrareal numbers if there exists $\beta \in R^*$ such that $f \leqslant \beta$ for all $f \in A^*$ then A^* is said to be bounded above and β is said to be an *upper bound* of A^*. Similarly a definition of A^* being bounded below may be introduced. When A^* is both bounded above and below then we simply say that A^* is a *bounded set* of ultra real numbers. If α be an upper bound of A^* and $\alpha \leqslant$ every upper bound of A^* then α is called the supremum of A^* which is indicated by $\alpha = \text{Sup } A^*$. Similarly one may define $\text{Inf } A^*$.

Now we proceed to explain the concept of open interval, neighbourhood and limiting point.

$\{ x : x \varepsilon R^*. \ a < x < b \}$ is called an open interval in R^* and is denoted by (a, b). If both a and b are standard elements, then (a, b) is called a standard open interval.

If an ultrareal number $\alpha \varepsilon (a, b)$ then (a, b) is said to be an open *neighbourhood* of α.

α is said to be a *limiting point* of an infinite set A^* iff every neighbourhood of α contains an infinity of elements of A^*.

Having introduced these concepts for R^* we wish to prove Bolzano–Weierstrass theorem now but for this we need to establish the existence of Sup A^* for every bounded set A^* which we first establish below.

4. *Theorem 1 : If A^* be a set of ultrareal numbers bounded above by a standard element b, then Sup A^* exists.*

Proof: Let $A^* = \{f, g, h, \ldots, x, \ldots\}$ be bounded above by b. Then we have $F = \{ n : f(n) < b \} \varepsilon U$, $G = \{ n : g(n) < b \} \varepsilon U$, $H = \{ n : h(n) < b \} \varepsilon U$ and we have similar relations for all other elements of A^*. Let $K = F \cap G \cap H \cap \ldots$ Then $K = \{ n : x(n) < b$ for all $x \varepsilon A^* \} \varepsilon U$. For a *fixed* $n \varepsilon K$ we have a set of real numbers.

$A^*n = \{f(n), g(n), h(n), \ldots, x(n), \ldots\} = \{ x(n) : x \varepsilon A^* \}$ which is bounded above by b. Hence, by Dedekind completeness property of R, Sup A^*n exists. Let $\alpha(n) =$ Sup A^*n. We get similar result for all elements of K. Let $\alpha = \{\alpha(n) : n \varepsilon N\}$ We hold that $\alpha =$ Sup A^*. For, we first find that for every element x of A^*, $\{ n : x(n) \leqslant \alpha(n) \} = K \varepsilon U$. Also for any upper bound β of A^* $x \leqslant \beta$ for all $x \varepsilon A^*$, *i.e.*, $\{ n : x(n) \leqslant \beta(n) \} \varepsilon U$. But $\alpha(n)$ is Sup A^*n so that $\{ n : \alpha(n) \leqslant \beta(n) \} \varepsilon U$, which means $\alpha \leqslant \beta$. Hence $\alpha =$ Sup A^* exists.

Lastly we prove the *Bolzano-Weierstrass* theorem below.

5. *Theorem 2 : Every bounded infinite set of finite elements in R^* has a limiting point in R^*.*

Proof: Let A^* be an infinite set of finite elements such that for all $x \varepsilon A^*$, $a < x < b$, where a and b are two standard elements. As in the previous theorem for a fixed $n \varepsilon N$ we have $A^*n = \{ x(n) : x \varepsilon A^* \}$ which is a set of real numbers.

We have seen in theorem 1 that Sup $A^* = \alpha$ exists and, for a fixed $n \varepsilon K$, $\alpha(n)$ is Sup A^*n. Hence infinity of elements of A^*n lie in every neighbourhood $(\alpha(n) - t, \alpha(n) + t)$ of $\alpha(n)$. Thus we have an infinity of members of A^* which lie in every open interval $(\alpha - t, \alpha + t)$ of α. Hence α is a limiting point of A^*.

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On the solution of certain integral equations involving Hypergeometric function

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1. Recently Srivastava [1] has obtained the inversion formulae for certain integral transforms involving Jacobi polynomials as their kernels by making use of a result of Tranter [2] and two other results which are the special cases of the well known Weber-Schafheitlin integral [3, p. 401].

The object of this paper is to obtain the solution of an integral equation involving hypergeometric function as kernel. As particular cases, we deduce the inversion formulae for certain integral transforms involving Jacobi polynomials as kernels which cover the cases of Srivastava [1].

2. We prove the following theorems

Theorem : If

$$\phi(x) = \frac{\Gamma\{(\mu+\nu+a-b+2)/2\}\, x^{-\mu-a+b-2}}{2^{-a+b-1}\,\Gamma\{(-\mu+\nu-a+b)/2\}\,\Gamma(\mu+1)} \int_0^x u^{\mu+1} \cdot$$

$$ {}_2F_1\left(\frac{\mu+\nu+a-b+2}{2}, \frac{\mu-\nu+a-b+2}{2}; \mu+1; u^2/x^2\right)\psi(u)\,du$$

$$+\frac{\Gamma\{(\mu+\nu+a-b+2)/2\}\, x^{\nu}}{2^{-a+b-1}\,\Gamma\{(\mu-\nu-a+b)/2\}\,\Gamma(\nu+1)}\int_x^{\infty} u^{-\nu-a+b-1}$$

$$\cdot\, {}_2F_1\left(\frac{\mu+\nu+a-b+2}{2}, \frac{-\mu+\nu+a-b+2}{2}; \nu+1;\, x^2/u^2\right)\psi(u)\,du; \quad (2\cdot1)$$

then

$$(i)\;\; \psi(x) = \frac{\Gamma\{(\mu+\nu-a+b)/2\}\, x^{-\nu+a-b}}{2^{a-b}\,\Gamma\{(\mu-\nu+a-b+2)/2\}\,\Gamma(\nu)}\int_0^x {}_2F_1\left(\frac{\mu+\nu-a+b}{2},\right.$$

$$\left.\frac{-\mu+\nu-a+b}{2}\; \nu;\, u^2/x^2\right) d\,[u^{\nu}\,\phi(u)] + \frac{\Gamma\{(\mu+\nu-a+b)/2\}}{\Gamma\{(-\mu+\nu+a-b)/2\}}$$

$$\cdot\,\frac{x^{u}}{2^{a-b}\,\Gamma(\mu+1)}\int_x^{\infty} u^{-\mu-\nu+a-b}\, {}_2F_1\left(\frac{\mu+\nu-a+b}{2}, \frac{\mu-\nu-a+b+2}{2};\right.$$

$$\left.\mu+1;\, x^2/u^2\right) d\,[u^{\nu}\,\phi(u)], \quad (2\cdot2)$$

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provided

$$(i)\ \nu > -\mu + a - b, \quad a < b < a + 1, \tag{2·3}$$

$$(ii) \int_0^\infty t\,|\,\psi(t)\,|\,dt \quad \text{and} \int_0^\infty t^{-\nu+1}\left|\frac{d}{dt}\,\{t^\nu\ \phi(t)\}\right| dt, \tag{2·4}$$

are convergent,

$$(iii)\ \frac{d}{dt}\,\{t^\nu\ \phi(t)\} \text{ is continuous ;} \tag{2·5}$$

and

$$(ii)\ \psi(x) = \frac{-\Gamma\{(\mu+\nu-a+b+2)/2\}\ x^{-\nu+a-b-2}}{2^{a-b}\,\Gamma\{(\mu-\nu+a-b)/2\}\,\Gamma(\nu+2)}\int_0^x u^{2\nu+2}$$

$${}_2F_1\left(\frac{\mu+\nu-a+b+2}{2},\ \frac{-\mu+\nu-a+b+2}{2};\ \nu+2\ ;\ u^2/x^2\right) d[u^{-\nu}\phi(u)]$$

$$-\frac{\Gamma\{(\mu+\nu-a+b+2)/2\}\ x^{\mu}}{2^{a-b}\,\Gamma\{(-\mu+\nu+a-b+2)/2\}\,\Gamma(\mu+2)}\int_x^\infty u^{-\mu+\nu+a-b}$$

$${}_2F_1\left(\frac{\mu+\nu-a+b+2}{2},\ \frac{\mu-\nu-a+b}{2};\ \mu+1\ ;\ x^2/u^2\right) d[u^{-\nu}\ \phi(u)], \tag{2·6}$$

provided

$$(i)\ \nu > -\mu - a + b - 2,\ a < b < a + 1, \tag{2·7}$$

$$(ii) \int_0^\infty t\,|\,\psi(t)\,|\,dt \quad \text{and} \int_0^\infty t^{\nu+1}\left|\frac{d}{dt}\,\{\,t^{-\nu}\ \phi(t)\,\}\right| dt, \tag{2·8}$$

are convergent,

$$(iii)\ \frac{d}{dt}\,\{\,t^{-\nu}\ \phi(t)\,\} \text{ is continuous.} \tag{2·9}$$

3. The proof of the theorem is as below.

Let

$$\phi(x) = \int_0^\infty y^a\,J_\nu(xy)\,f(y)\,dy. \tag{3·1}$$

and

$$\psi(x) = \int_0^\infty y^b\,J_\mu(xy)\,f(y)\,dy. \tag{3·2}$$

Inverting (3·2) by Hankel's inversion theorem [4], we obtain

$$f(y) = y^{-b+1}\int_0^\infty u\,J_\mu(uy)\ \psi(u)\,du,$$

and on substituting the value of $f(y)$ in (3·1), we obtain

$$\begin{aligned}\phi(x) &= \int_0^\infty y^{a-b+1}\,J_\nu(xy)\,dy\int_0^\infty u\,J_\mu(yu)\,\psi(u)\,du\\ &= \int_0^\infty u\,\psi(u)\,du\int_0^\infty y^{a-b+1}\,J_\mu(uy)\,J_\nu(xy)\,dy\\ &= \frac{\Gamma\{(\mu+\nu+a-b+2)/2\}\ x^{-\mu-a+b-2}}{2^{-a+b-1}\,\Gamma\{(-\mu+\nu-a+b)/2\}\,\Gamma(\mu+1)}\int_0^x u^{\mu+1}\end{aligned}$$

$$
{}_2F_1\left(\frac{\mu+\nu+a-b+2}{2}, \frac{\mu-\nu+a-b+2}{2}; \mu+1; u^2/x^2\right)\psi(u)\,du
$$

$$
+\frac{\Gamma\{(\mu+\nu+a-b+2)/2\}\,x^{\nu}}{2^{-a+b-1}\,\Gamma\{(\mu-\nu-a+b)/2\}\,\Gamma(\nu+1)}\int^{\infty} u^{-\nu-a+b-1}
$$

$$
{}_2F_1\left(\frac{\mu+\nu+a-b+2}{2}, \frac{-\mu+\nu+a-b+2}{2}; \nu+1;\ x^2/u^2\right)\psi(u)\,du, \quad (3\cdot3)
$$

provided

(i) $\nu > -\mu - a + b - 2,\ a < b$,

(ii) $\int_0^1 t^{\mu+b}\,|f(t)|\,dt$ and $\int_1^{\infty} t^{b-1/2}\,|f(t)|\,dt$ are convergent.

(iii) $\int_0^{\infty} t\,|\psi(t)|\,dt$ is convergent,

where we have used the result [3, p. 401] to evaluate y integral. The change of order of integration is justified under the conditions mentioned above.

From (3·1), we obtain

$$
x^{-\nu}\frac{d}{dx}\{x^{\nu}\phi(x)\} = \int_0^{\infty} y^{a+1} J_{\nu-1}(xy) f(y)\,dy,
$$

and then by Hankel's inversion theorem,

$$
f(y) = y^{-a}\int_0^{\infty} u^{-\nu+1} J_{\nu-1}(yu)\,d[u^{\nu}\phi(u)].
$$

on substituting this value of $f(y)$ in (3·2), we obtain

$$
\begin{aligned}
(i)\ \psi(x) &= \int_0^{\infty} y^{-a+b} J_{\mu}(xy)\,dy \int_0^{\infty} u^{-\nu+1} J_{\nu-1}(yu)\,d[u^{\nu}\phi(u)] \\
&= \int_0^{\infty} u^{-\nu+1}\,d[u^{\nu}\phi(u)]\int_0^{\infty} y^{-a+b} J_{\mu}(xy) J_{\nu-1}(uy)\,dy \\
&= \frac{\Gamma\{(\mu+\nu-a+b)/2\}\ x^{-\nu+a-b}}{2^{a-b}\,\Gamma\{(\mu-\nu+a-b+2)/2\}\,\Gamma(\nu)}\int_0^{x} {}_2F_1\left(\frac{\mu+\nu-a+b}{2},\right. \\
&\left.\frac{-\mu+\nu-a+b}{2}; \nu; u^2/x^2\right) d[u^{\nu}\phi(u)] + \frac{\Gamma\{(\mu+\nu-a+b)/2\}}{\Gamma\{(-\mu+\nu+a-b)/2\}} \\
&\frac{x^{\mu}}{2^{a-b}\,\Gamma(\mu+1)}\int_x^{\infty} u^{-\mu-\nu+a-b}\,{}_2F_1\left(\frac{\mu+\nu-a+b}{2}, \frac{\mu-\nu-a+b+2}{2};\right. \\
&\left.\mu+1; x^2/u^2\right) d[u^{\nu}\phi(u)],
\end{aligned} \quad (3\cdot4)
$$

provided

(i) $\nu > -\mu + a - b,\ \ b < a + 1$,

(ii) $\int_0^1 t^{\nu+a}\,|f(t)|\,dt$ and $\int_1^{\infty} t^{a+1/2}\,|f(t)|\,dt$ are convergent,

(iii) $\int_0^{\infty} t^{-\nu+1}\left|\frac{d}{dt}\{t^{-\nu}\phi(t)\}\right| dt$ is convergent

(iv) $\dfrac{d}{dt}\{t^{\nu}\,\phi(t)\}$ is continuous.

where we have used the result [3]. The change of order of integration is justified under the above conditions.

If we write (3·1) in the form

$$\frac{d}{dt}\{x^{-\nu}\,\phi(x)\} = -\,x^{-\nu}\int_0^{\infty} y^{a+1}\,J_{\nu+1}(xy)\,f(y)\,dy,$$

we obtain, in a similar manner

$$(ii)\qquad \psi(x) = \frac{-\,\Gamma\{(\mu+\nu-a+b+2)/2\}\;x^{-\nu+a-b-2}}{2^{a-b}\,\Gamma\{(\mu-\nu+a-b)/2\}\,\Gamma(\nu+2)}\int_0^{x} u^{2\nu+2}$$

$$ {}_2F_1\left(\frac{\mu+\nu-a+b+2}{2},\ \frac{-\mu+\nu-a+b+2}{2};\ \nu+2;\ u^2/x^2\right)d[u^{-\nu}\,\phi(u)]$$

$$-\frac{\Gamma\{(\mu+\nu-a+b+2)/2\}\;x^{\mu}}{2^{a-b}\,\Gamma\{(-\mu+\nu+a-b+2)/2\}\,\Gamma(\mu+1)}\int_x^{\infty} u^{-\mu+\nu+a-b}$$

$$ {}_2F_1\left(\frac{\mu+\nu-a+b+2}{2},\ \frac{\mu-\nu-a+b}{2};\ \mu+1;\ x^2/u^2\right)d[u^{-\nu}\,\phi(u)], \tag{3·5}$$

provided

(i) $\nu > -\mu - a + b - 2,\ b < a + 1,$

(ii) $\displaystyle\int_0^1 t^{\nu+a+1}\,|f(t)|\,dt$ and $\displaystyle\int_1^{\infty} t^{a+1/2}\,|f(t)|\,dt$ are convergent,

(iii) $\displaystyle\int_0^{\infty} t^{\nu+1}\,\left|\frac{d}{dt}\{t^{-\nu}\,\phi(t)\}\right|\,dt$ is convergent,

(iv) $\dfrac{d}{dt}\{t^{-\nu}\,\phi(t)\}$ is continuous.

Hence the theorem.

4. *Particular Cases.* In this section we deduce the following two particular cases of the theorem of section 2.

Case (*i*). Take $\mu = -2m + a - b$, where m is a prositive integer, then the solution of the integral equation

$$\phi(x) = \frac{\Gamma(\nu-m+a-b+1)\quad x^{-\nu+2m}}{2^{-a+b-1}\,\Gamma(m-a+b)\,\Gamma(\nu-2m+a-b+1)}\int_0^{x} u^{\nu-2m+a-b+1}$$

$$(x^2-u^2)^{-a+b-1}\,F_m(\nu-2m,\ \nu-2m+a-b+1;\ u^2/x^2)\,\psi(u)\,du, \tag{4·1}$$

is given by

$$(i)\quad \psi(x) = \frac{\Gamma(\nu-m)\;x^{-\nu+a-b}}{2^{a-b}\,\Gamma(-m+a-b+1)\,\Gamma(\nu)}\int_0^{x} {}_2F_1(\nu-m,\ m-a+b;\ u^2/x^2)$$

$$d\,[u^{\nu}\,\phi(u)] + \frac{\Gamma(\nu-m)\quad x^{\nu-2m+a-b}}{2^{a-b}\,\Gamma(\nu-2m+a-b+1)\,\Gamma(m)}\int_x^{\infty} u^{-2\nu+2m}$$

$$F_{m-1}(\nu-2m+1,\ \nu-2m+a-b+1;\ x^2/u^2)\,d[u^{\nu}\,\phi(u)],$$

provided $\nu > m$, $a < b < a + 1$ and the conditions (2·4) and (2·5) are satisfied,

and

$$(ii) \qquad \psi(x) = \frac{-\Gamma(\nu - m + 1)\, x^{-\nu+a-b-2}}{2^{a-b}\,\Gamma(-m + a - b)\,\Gamma(\nu + 2)} \int_0^x u^{2\nu+2}\, {}_2F_1\,(\nu - m + 1,$$

$$m - a + b + 1\, ;\, \nu + 2,\, u^2/x^2)\; d[u^{-\nu}\,\phi(u)]\; \frac{-\Gamma(\nu - m + 1)}{2^{a-b}\,\Gamma(m + 1)}$$

$$\Gamma\,\frac{x^{\nu-2m+a-b}}{(\nu - 2m + a - b + 1)} \int_x^\infty u^{\nu+1}\, F_m(\nu - 2m + 1,\, \nu - 2m + a - b + 1\, ;\, x^2/u^2)$$
$$d[u^{-\nu}\,\phi(u)], \qquad (4{\cdot}3)$$

provided $\nu > m - a + b - 1$, $a < b < a + 1$ and the conditions (2·8) and (2·9) are satisfied.

For $a=1$, $b=k + 1$, $\nu=\lambda + 2m + k$, $\phi(x)=x^{-\lambda-k}\,\Phi(x)\,A_m$ and $\psi(x)=x^{\lambda}\,\psi(x)$, where

$$A_m = \frac{\Gamma(\lambda + m + 1)}{2^{k-1}\,\Gamma(m + k)\,\Gamma(\lambda + 1)},$$

the equations (4·1) and (3·2) reduce to

$$\phi(x) = \int_0^x u^{2\lambda+1}\,(x^2 - u^2)^{k-1}\, F_m(\lambda + k,\, \lambda + 1\, ;\, u^2/x^2)\, \Psi(u)\, du, \qquad (4{\cdot}4)$$

and

$$\Psi(x) = \frac{2\Gamma(\lambda + m + k)\,\Gamma(\lambda + m + 1)}{\{(\lambda + 1)\}^2\,\Gamma(m)\,\Gamma(m + k)} \Bigg[\frac{\Gamma(\lambda + 1)\,\Gamma(m)}{\Gamma(\nu + 2m + k)\,\Gamma(-m - k + 1)}$$

$$\cdot \int_0^x \frac{H_{m-1}\,(\lambda + k + 1,\, \lambda + 1\, ;\, x^2/u^2)\; d[u^{2m}\,\Phi(u)]}{u^{2(\lambda+m+k)}}$$

$$+ \int_x^\infty \frac{F_{m-1}\,(\lambda + k + 1,\, \lambda + 1,\, x^2/u^2)\; d[u^{2m}\,\phi(u)]}{u^{2(\lambda+m+k)}}\Bigg], \qquad (4{\cdot}5)$$

provided $\lambda > -1$, $0 < k < 1$ and the conditions (2·4) and (2·5) are satisfied where H_m is a Jacobi function of the second kind defined by the relation of the form

$$H_m(\lambda + k,\, \lambda\, ;\, r^2) = r^{-2m-2\lambda}\,(r^2 - 1)^{-k}\, {}_2F_1\,(m + 1, m + \lambda\, ;\, \lambda + 2m + k + 1\, ;\, 1/r^2),$$

and F_m is a Jacobi polynomial [5]. This is a solution obtained by Srivastava [1, eq. (2·4)].

Case (*ii*). Take $\mu = \nu + 2m - a + b$, where m is a positive integer or zero, then the solution of the integral equation

$$\phi(x) = \frac{\Gamma(\nu + m + 1)\quad x^{\nu}}{2^{-a+b-1}\,\Gamma(m - a + b)\,\Gamma(\nu + 1)} \int_x^\infty u^{-\nu+a-b+1}\,(u^2 - x^2)^{-a+b-1}$$

$$\cdot F_m\,(\nu - a + b,\, \nu + 1,\, x^2/u^2)\, \psi(u)\, du, \qquad (4{\cdot}6)$$

is given by

$$(i)\ \psi(x) = \frac{\Gamma(\nu - m - a + b)}{2^{a-b}\,\Gamma(m+1)} \frac{x^{-\nu+a-b}}{\Gamma(\nu)} \int_0^x F_m\,(\nu - a + b,\ \nu\ ;\ u^2/x^2)\ d[u^\nu\,\phi(u)]$$

$$+ \frac{\Gamma(\nu + m - a + b)\quad x^{\nu+2m-a+b}}{2^{a-b}\,\Gamma(-m + a - b)\,\Gamma(\nu + 2m - a + b + 1)} \int_x^\infty u^{-2\nu-2m}\,(u^2 - x^2)^{a-b}$$

$$\cdot\ {}_2F_1\,(m+1,\ m+\nu\ ;\ \nu + 2m - a + b + 1\ ;\ \ x^2/u^2)\ d[u^\nu\,\phi(u)], \tag{4·7}$$

provided $\nu > a - b,\ a < b < a + 1$ and the conditions (2·4) and (2·5) are satisfied;

$$(ii)\qquad \psi(x) = \frac{-\Gamma(\nu + m - a + b + 1)\ x^{-\nu+a-b}\ 2}{2^{a-b}\,\Gamma(m)\,\Gamma(\nu+2)} \int_0^x u^{2\nu+2}\,F_{m-1}\,(\nu - a + b + 2,$$

$$\nu + 2,\ u^2/x^2)\ d[u^{-\nu}\,\phi(u)] - \frac{\Gamma(\nu + m - a + b + 1)\quad x^{\nu+2m-a+b}}{2^{a-b}\,\Gamma(-m + a - b + 1)\,\Gamma(\nu + 2m - a + b + 1)}$$

$$\cdot \int_x^\infty u^{-\mu+\nu+a-b}\ {}_2F_1\,(\nu + m - a + b + 1,\ m - a + b\ ;\ \nu + 2m - a + b + 1;\ x^2/u^2)$$
$$d[u^{-\nu}\,\phi(u)]\ . \tag{4·8}$$

provided $\nu > -1,\ a < b < a + 1$ and the conditions (2·8) and (2·9) are satisfied.

For $a = 1,\ b = k + 1,\ \nu = \lambda,\ \phi(x) = x^\nu\,\Phi(x)\ A_m$, and $\psi(x) = x^{-\lambda-k}\,\Psi(x)$, the equations (4·6) and (4·7) reduce to

$$\phi(x) = \int_x^\infty u^{-2\lambda-2k+1}\,(u^2 - k^2)^{k-1}\,F_m\,(\lambda + k,\ \lambda + 1\ ;\ x^2/u^2)\ \Psi(u)\ du \tag{4·9}$$

and

$$\Psi(x) = \frac{2\Gamma(\lambda + m + 1)\quad \Gamma(\lambda + m + k)}{\Gamma(\lambda)\,\Gamma(\lambda + 1)\,\Gamma(m+1)\,\Gamma(m + k)} \int_0^x F_m\,(\lambda + k,\ \lambda,\ x^2/u^2)\ d[u^{2\lambda}\,\phi(u)] +$$

$$\frac{\Gamma(\lambda)\ \Gamma(m+1)}{\Gamma(\lambda + 2m + k + 1)\ \Gamma(-m - k)} \int_x^\infty H_m(\lambda + k,\ \lambda,\ u^2/x^2)\ d[u^{2\lambda}\ \Phi(u)], \tag{4·10}$$

provided $\lambda > -1,\ 0 < k < 1$ and the conditions (2·8) and (2·9) are satisfied. This is another solution obtained by Srivastava [1, eq. (2·2)].

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Applications of Jacobi polynomials to non-linear differential equation associated with confluent hypergeometric function

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Abstract

By the application of linear Jacobi polynomial approximation, we obtain the solution of the differential equation

$$\ddot{x} + \omega_0^2 \, x^r \, {}_1F_1 (\gamma \, ; \delta \, ; cx^s) = 0$$

where r and s are positive integers and ${}_1F_1(\gamma, \delta \, ; x)$ is the Kummer's confluent hypergeometric function. The approximate solutions of differential equations containing an exponential function, a binomial and a Bessel function of the first kind as non-linearities are derived from the general result. The results obtained are of general character and include, as particular cases, some of the results given earlier by the authors and Garde.

1. Introduction

In 1959, Denman[2] proved that an amplitude-dependent approximation to the frequency of the simple pendulum may be obtained by the application of a linear Tchebycheff polynomial approximation to sin θ in the interval $(-A, A)$, where A is the amplitude of the motion. In 1964, Denman and Howard[3] and Denman and Liu[4] have applied the ultraspherical polynomials which include the Legendre polynomials, the Tchebycheff polynomials of the first and second kind, and the Taylor series as particular cases, to the above problem. In 1965, Garde[7] has applied Gegenbauer polynomials to some forced oscillation problems. In 1967[8] Jacobi polynomials were used to obtain a linear amplitude dependent approximation for the purpose of linearisation of the differential equation with cubic non linearity.

Recently in[1J] the authors have applied the Jacobi polynomials to obtain the amplitude dependent linear approximate solution of the differential equation

$$\ddot{x} + ax + bx^s = 0 \tag{1 1}$$

where s is a positive integer, subject to the initial conditions $x = A$, $\dot{x} = 0$ at $t = 0$, A being the amplitude of the motion. The results obtained were found to agree fairly with the known exact results available for cases $s = 1$ and $s = 3$ and it was observed that the approximation can be improved by suitable choice of the two parameters α and β in the weight function.

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The success of the application of Jacobi polynomials to obtain the solution of (1·1) has led the authors to consider the solution a more general differential equation

$$\ddot{x} + \omega_0^2 x^r {}_1F_1(\gamma ; \delta ; cx^s) = 0 \tag{1·2}$$

where r and s are positive integers and ${}_1F_1(\gamma ; \delta ; x)$ denotes the Kummer's confluent hypergeometric function defined by

$${}_1F_1(\gamma ; \delta ; z) = \sum_{n=0}^{\infty} \frac{(\gamma)_n z^n}{(\delta)_n\, n!}. \tag{1·3}$$

The symbol $(\gamma)_n$ represents

$$\frac{\Gamma(\gamma + n)}{\Gamma(\gamma)} = \gamma(\gamma + 1) \ldots . (\gamma + n - 1) ; (\gamma)_0 = 1. \tag{1·4}$$

In (1 3), $\delta \neq$ zero or a negative integer. The series (1·3) is absolutely convergent for all real or complex values of γ, δ and z. The initial conditions of motion are $x = A$ and $\dot{x} = 0$ at, $t = 0$, A being the amplitude of motion, under which the solution of (1·2) will be obtained. The main result obtained generalizes the results given earlier by Garde [8, p. 118(61)] and the authors[1]. Most of the results obtained in this paper are not recorded in literature.

2. *Jacobi polynomials and linear approximation.*

Jacobi polynomials are the sets of polynomials orthogonal in the interval $(-1, 1)$ with respect to the weight function $(1 - x)^\alpha (1 + x)^\beta$, where $Re\ \alpha > -1$ and $Re\ \beta > -1$, and may be defined by [6, p. 254]

$$P_n^{(\alpha, \beta)}(x) = \frac{(1 + \alpha)_n}{n!}\, {}_2F_1\left(-n, \frac{\alpha + \beta + n + 1}{1 + \alpha} ; \frac{1 - x}{2}\right), \tag{2·1}$$

where ${}_2F_1$ is the Gauss's hypergeometric function [10, p. 7]. Tchebycheff polynomials, Legendre polynomials and Ultraspherical polynomials are particular cases of Jacobi polynomials [6, pp. 265–269].

In the interval $(-A, A)$, Jacobi polynomials are defined as the sets of polynomials orthogonal in this interval with respect to the weight function $(1 - x/A)^\alpha$ $(1 + x/A)^\beta$. This gives rise to $P_n^{(\alpha, \beta)}(x/A)$.

For a function $f(x)$, which can be expanded in terms of Jacobi polynomials in the interval $(-A, A)$, we obtain

$$f(x) = \sum_{n=0}^{\infty} a_n^{(\alpha, \beta)} P_n^{(\alpha, \beta)}(x/A) \tag{2·2}$$

where the coefficients $a_n^{(\alpha, \beta)}$ are given by

$$a_n^{(\alpha, \beta)} = \frac{\int_{-1}^{1} f(Ax)\, P_n^{(\alpha, \beta)}(x)\, (1 - x)^\alpha (1 + x)^\beta\, dx}{\int_{-1}^{1} [P_n^{(\alpha, \beta)}(x)]^2 (1 - x)^\alpha (1 + x)^\beta\, dx} \tag{2·3}$$

If the series (2·2) is truncated after the second term, we obtain a linear approximation

$$f_*(x) = a_0^{(\alpha,\beta)} P_0^{(\alpha,\beta)} (x/A) + a_1^{(\alpha,\beta)} P_1^{(\alpha,\beta)} (x/A),$$

where star indicates approximation.

3. *Results required in the sequel.*

In the investigations that follow we shall require the following integrals [12, p. 466], [10, p. 261], [1, p. 160].

$$\int_{-1}^{1} x^s(1-x)^\alpha (1+x)^\beta P_n^{(\alpha,\beta)}(x)\, dx$$

$$= \frac{2^{n+\alpha+\beta+1}\, s!\, \Gamma(\alpha+n+1)\, \Gamma(\beta+s+1)}{n!\,(s-n)!\, \Gamma(n+s+\alpha+\beta+2)}$$

$$\times\ {}_2F_1\left(\begin{matrix} n-s,\ \alpha+n+1 \\ -\beta-s \end{matrix} ; -1\right), \text{ for } s > n \tag{3·1}$$

$$= 0 \text{ for } s < n \tag{3·2}$$

$$= \frac{2^{\alpha+\beta+n+1}\, \Gamma(1+\alpha+n)\, \Gamma(1+\beta+n)}{1(\alpha+\beta+2n+2)}, \text{ for } s = n. \tag{3·3}$$

The following obvious properties of Jacobi polynomials, confluent hypergeometric function ${}_1F_1$ and ordinary Bessel function $J_\nu(x)$ will be made use of:

$$P_0^{(\alpha,\beta)}(x) = 1, \quad P_1^{(\alpha,\beta)}(x) = \frac{\alpha-\beta}{2} + \frac{2+\alpha+\beta}{2}\, x \tag{3·4}$$

$${}_1F_1(\gamma\, ;\, \gamma\, ;\, x) = e^x \tag{3·5}$$

$$\lim_{\delta\to\infty}\ {}_1F_1(\gamma : \delta\, ;\, \delta x) = {}_1F_0(\gamma\, ;\, x) \tag{3·6}$$

$$= (1-x)^{-\gamma} \tag{3·7}$$

$$\lim_{\gamma\to\infty}\ {}_1F_1(\gamma\, ;\, \delta\, ;\, x/\gamma) = {}_0F_1(-\, ;\, \delta\, ;\, x) \tag{3·8}$$

$${}_0F_1(-\, ;\, \delta+1\, ;\, -\tfrac{1}{4}x^2) = \Gamma(\delta+1)\, (\tfrac{1}{2}x)^{-\delta} J_\delta(x) \tag{3·9}$$

$$\left(\frac{\pi x}{2}\right)^{\frac{1}{2}} J_{\frac{1}{2}}(x) = \sin x \tag{3·10}$$

4. *Applications of Jacobi polynomials to non-linear differential equation.*

In this section we propose to solve the differential equation

$$\ddot{x} + f(x) = 0 \tag{4·1}$$

where

$$f(x) = \omega_0^2\, x^r\, {}_1F_1(\gamma\, ;\, \delta,\, cx^s)$$

by making use of the linear Jacobi polynomial's approximation of $f(x)$.

By § 2, the linear Jacobi polynomial approximation of $f(x)$ gives

$$f_*(x) = [\omega_0^2\, x^r\, {}_1F_1(\gamma\, ;\, \delta\, ;\, cx^s)]_*$$

$$= a_0^{(\alpha,\beta)} P_0^{(\alpha,\beta)}(x/A) + a_1^{(\alpha,\beta)} P_1^{(\alpha,\beta)}(x/A) \tag{4·2}$$

where

$$a_0^{(\alpha,\beta)} = \frac{\Gamma(\alpha+\beta+2)\, A^r\, \omega_0^2}{2^{\alpha+\beta+1}\,\Gamma(\alpha+1)\,\Gamma(\beta+1)}$$

$$\times \int_{-1}^{1} x^r (1-x)^\alpha (1+x)^\beta \; {}_1F_1(\gamma\,;\,\delta\,;\,c\,A^s\,x^s)\; P_0^{(\alpha,\beta)}(x)\, dx \tag{4·3}$$

and

$$a_1^{(\alpha,\beta)} = \frac{(\alpha+\beta+3)\,\Gamma(\alpha+\beta+2)}{2^{\alpha+\beta+1}\,\Gamma(\alpha+2)\,\Gamma(\beta+2)}\; \omega_0^2\, A^r$$

$$\times \int_{-1}^{1} x^r (1-x)^\alpha (1+x)^\beta \; P_1^{(\alpha,\,\beta)}(x)\; {}_1F_1(\gamma\,;\,\delta\,;\,c\,A^s\,x^s)\, dx \tag{4·4}$$

on using (3·1), and (3·3), we find that

$$a_0^{(\alpha,\beta)} = \frac{\alpha-\beta}{\alpha+\beta+2}\, A^r\, \omega_0^2 \sum_{j=0}^{\infty} \frac{(\gamma)_j\, C^j A^{sj}\, \Gamma(\alpha+\beta+3)\,\Gamma(\beta+r+sj+1)}{(\delta)_j\, j\,!\,\Gamma(\beta+1)\,\Gamma(\alpha+\beta+r+sj+2)}$$

$$\times \frac{}{\alpha-\beta}\; {}_2F_1\left(\begin{matrix} -r-sj,\ \alpha+1 \\ -\beta-r-sj \end{matrix}\ ;\ -1\right) \tag{4·5}$$

and

$$a_1^{(\alpha,\beta)} = (2A^r\,\omega_0^2/\alpha+\beta+2) \sum_{j=0}^{\infty} \frac{(\gamma)_j\, c^j A^{sj}\,(r+sj)\,\Gamma(\alpha+\beta+4)}{(\delta)_j\, j\,!\,\Gamma(2+\beta)\,\Gamma(r+sj+\alpha+\beta+3)}$$

$$\times\; {}_2F_1\left(\begin{matrix} 1-r-sj,\ \alpha+2 \\ -\beta-r-sj \end{matrix}\ ;\ -1\right).$$

On applying (3·4), it follows that

$$f_*(x) = [\omega_0^2\, x^r\; {}_1F_1(\gamma\,;\,\delta\,;\,cx^s)]_* = \lambda^2_{r,s}\, x + \frac{(\alpha-\beta)A}{\alpha+\beta+2}\left[\ \lambda^2_{r,s} + 1^2_{1,r,s}\right] \tag{4·6}$$

where

$$\lambda^2_{r,s} = \omega_0^2\, A^{r-1} \sum_{j=0}^{\infty} \frac{(r+sj)\,(\gamma)_j\, C^j\, A^{sj}}{(\delta)\; jj\,!}$$

$$\times \frac{\Gamma(\alpha+\beta+4)\,\Gamma(\beta+r+sj+1)}{\Gamma(\beta+2)\,\Gamma(r+sj+\alpha+\beta+3)}\; {}_2F_1\left(\begin{matrix} 1-r-sj,\ \alpha+2 \\ -\beta-r-sj \end{matrix}\ ;\ -1\right) \tag{4·7}$$

and

$$\lambda^2_{1,r,s} = \frac{A^{r-1}\,\omega_0^2}{\alpha-\beta} \sum_{j=0}^{\infty} \frac{(\gamma)_j\,\Gamma(\alpha+\beta+3)\,\Gamma(\beta+r+sj+1)\,C^j A^{sj}}{(\delta)_j\, j\,!\,\Gamma(1+\beta)\,\Gamma(\alpha+\beta+r+sj+2)}$$

$$\times_{\,2} \left(\begin{matrix} r-sj,\ \alpha+1 \\ -\beta-r-sj \end{matrix}\ ;\ -1\right) \tag{4·8}$$

Replacing $f(x)$ by its approximation $f_*(x)$, (4·1) transforms into

$$\ddot{x} + \lambda_{r,s}^2 x = \frac{(\beta - \alpha) A}{\alpha + \beta + 2}\left[\lambda_{r,s}^2 + \lambda_{1,r,s}^2 \right] \tag{4·9}$$

The approximate solution of (3·1) subject to the initial conditions $x = A$ and $\dot{x} = 0$ at $t = 0$ is thus

$$x_* = \left[A - \frac{(\beta - \alpha)A}{\alpha + \beta + 2}\left(1 + \lambda_{1,r,s}^2 / \lambda_{r,s}^2 \right)\right] \mathrm{Cos}\ \lambda_{r,s}\, t + \frac{(\beta - \alpha)A}{\alpha + \beta + 2}\left(1 + \lambda_{1,r,s}^2 / \lambda_{r,s}^2 \right) \tag{4·10}$$

and the approximate period is given by

$$T_* = 2\pi/\lambda_{r,s} \tag{4·11}$$

5. *Particular cases.*

(*i*) *General exponential non-linearity.* When $\gamma = \delta$, then using (3·5) we see that the approximate solution of the non-linear differential equation

$$\ddot{x} + \omega_0^2\, x^r \exp\,(cx^s) = 0 \tag{5·1}$$

is given by

$$x_* = \left[A - \frac{(\beta - \alpha)A}{\alpha + \beta + 2}\left(\lambda_{r,s}^{*2} + \lambda_{1,r,s}^{*2} \right) / \lambda_{r,s}^{*2} \right] \mathrm{Cos}\ \lambda_{r,s}^{*}\, t + \frac{(\beta - \alpha)A}{\alpha + \beta + 2}\left(1 + \lambda_{1,r,s}^{*2} / \lambda_{r,s}^{*2}\right), \tag{5·2}$$

where

$$\lambda_{r,s}^{*2} = \omega_0^2 A^{r-1} \sum_{j=0}^{\infty} \frac{(r + sj)\, C^j A^{sj}\, \Gamma(\alpha + \beta + 4)\, \Gamma(\beta + r + sj + 1)}{j\,!\ \Gamma(\beta + 2)\ \Gamma(r + sj + \alpha + \beta + 3)} \times {}_2F_1\left(\begin{matrix} 1 - r - sj,\ \alpha + 2 \\ -\beta - r - sj \end{matrix} ; -1 \right) \tag{5·3}$$

and

$$\lambda_{1,r,s}^{*2} = \frac{\omega_0^2 A^{r-1}}{\alpha - \beta} \sum_{j=0}^{\infty} \frac{\Gamma(\alpha + \beta + 3)\ \Gamma(\beta + r + sj + 1)\ C^j A^{sj}}{j\,!\ \Gamma(\beta + 1)\ \Gamma(\alpha + \beta + r + sj + 2)} \times {}_2F_1\left(\begin{matrix} -r - sj,\ \alpha + 1 \\ -\beta - r - sj \end{matrix} ; -1 \right) \tag{5·4}$$

The approximate period is given by

$$T_* = 2\pi/\lambda_{r,s}^* \tag{5·5}$$

(*ii*) *Binomial non linearity.* Applying (3·6) and (3·7), it follows that the approximate solution of the non-linear differential equation

$$\ddot{x} + \omega_0^2 \, x^r (1 - C \, x^s)^{-\gamma} = 0 \tag{5·6}$$

is given by

$$x_* = \left[A - \frac{(\beta - \alpha)A}{\alpha + \beta + 2} \left(1 + \lambda^{**2}_{1,r,s} \Big/ \lambda^{**2}_{r,s} \right) \right] \text{Cos} \, \lambda^{**}_{r,s} \, t$$

$$+ \frac{(\beta - \alpha)A}{\alpha + \beta + 2} \left(1 + \lambda^{**2}_{1,r,s} \Big/ \lambda^{**2}_{r,s} \right), \tag{5·7}$$

where

$$\lambda^{**2}_{r,s} = \omega_0^2 \, A^{r-1} \sum_{j=0}^{\infty} \frac{(r + sj) \, (\gamma)_j \, C^j A^{sj}}{j\,!}$$

$$\times \frac{\Gamma(\alpha + \beta + 4) \, \Gamma(\beta + r + sj + 1)}{\Gamma(\beta + 2) \, \Gamma(r + sj + \alpha + \beta + 3)} \; {}_2F_1 \left(\begin{matrix} 1 - r - sj, \; \alpha + 2 \\ - \beta - r - sj \end{matrix} ; - 1 \right) \tag{5·8}$$

and

$$\lambda^{**2}_{1,r,s} = \frac{A^{r-1} \, \omega_0^2}{\alpha - \beta} \sum_{j=0}^{\infty} \frac{(\gamma)_j \, \Gamma(\alpha + \beta + 3) \, \Gamma(\beta + r + sj + 1) \, C^j A^{sj}}{j\,! \, \Gamma(1 + \beta) \, \Gamma(\alpha + \beta + r + sj + 2)}$$

$$\times \; {}_2F_1 \left(\begin{matrix} - r - sj, \; \alpha + 1 \\ - \beta - r - sj \end{matrix} ; - 1 \right) \tag{5·9}$$

The approximate period is

$$T_* = 2\pi / \lambda^{**}_{r,s} \tag{5·10}$$

For $r = 1$, $\gamma = -1$, (5·7) and (5·10) reduce to the results given earlier by the authors[11].

(*iii*) *Bessel non-linearity.* On employing the formulae (3·8) and (3·9) it is found that the approximate solution of the following non-linear differential equation

$$\ddot{x} + \omega_0^2 \, 2^\delta \, \Gamma(\delta + 1) \, x^{r-\delta} \, J_\delta(x) = 0, \tag{5·11}$$

where $J_\delta(x)$ is the ordinary Bessel function of the first kind, is given by

$$x_* = \left[A - \frac{(\beta - \alpha)A}{\alpha + \beta + 2} \left(1 + \lambda^2_{1,r,2} \Big/ \lambda^2_{r,s} \right) \right] \text{Cos} \, \lambda_{r,2} \, t$$

$$+ \frac{(\beta - \alpha)A}{\alpha + \beta + 2} \left(1 + \lambda^2_{1,r,s} \Big/ \lambda^2_{r,s} \right), \tag{5·12}$$

where

$$\lambda_{r,2}^{2} = \omega_0^2 A^{r-1} \sum_{j=0}^{\infty} \frac{(r+2j)(-A^2)^j}{2^{2j}(\delta+1)_j j!}$$

$$\times \frac{\Gamma(\alpha+\beta+4)\,\Gamma(\beta+r+2j+1)}{\Gamma(\beta+2)\,\Gamma(r+2j+\alpha+\beta+3)}\, {}_2F_1\left(\begin{matrix}1-r-2j,\ \alpha+2\\ -\beta-r-2j\end{matrix};-1\right) \tag{5·13}$$

and

$$\lambda_{1,r,s}^{2} = \frac{A^{r-1}\omega_0^2}{\alpha-\beta} \sum_{r=0}^{\infty} \frac{\Gamma(\alpha+\beta+3)\,\Gamma(\beta+r+2j+1)(-A^2)^j}{2^{2j} j!(\delta+1)_j \Gamma(1+\beta)\,\Gamma(\alpha+\beta+r+2j+2)}$$

$$\times {}_2F_1\left(\begin{matrix}-r-2j,\ \alpha+1\\ -\beta-r-2j\end{matrix};-1\right) \tag{5·14}$$

The approximate period is given by

$$T_* = 2\pi/\lambda_{r,2} \tag{5·15}$$

If we take $r = 1$, $\delta=\frac{1}{2}$ in (5·11) and apply the Legendre's duplication formula for the gamma functions [5, p. 6] and (3·10), we find that the differential equation

$$\ddot{x} + \omega_0^2 \sin x = 0 \tag{5·16}$$

has the following approximate solution as obtained by Garde [8, p. 118(61)],

$$x_* = \left[A - \frac{(\beta-\alpha)A}{\alpha+\beta+2}\left(1+\lambda_{1,1,2}^{2} \Big/ \lambda_{1,2}^{2}\right)\right] \operatorname{Cos} \lambda_{1,2}\, t$$

$$+ \frac{(\beta-\alpha)A}{\alpha+\beta+2}\left(1+\lambda_{1,1,2}^{2} \Big/ \lambda_{1,2}^{2}\right), \tag{5·17}$$

and the approximate period is given by

$$T_* = 2\pi/\lambda_{1,2}, \tag{5·18}$$

where

$$\lambda_{1,2}^{2} = \omega_0^2 \sum_{j=0}^{\infty} \frac{(-A^2)^j\,\Gamma(\alpha+\beta+4)\,\Gamma(\beta+2j+2)}{\Gamma(\beta+2)\,\Gamma(\alpha+\beta+2j+4)(2j)!}$$

$$\times {}_2F_1\left(\begin{matrix}-2j,\ \alpha+2\\ -\beta-2j-1\end{matrix};-1\right) \tag{5·19}$$

and

$$\lambda_{1,1,2}^{2} = \frac{\omega_0^2}{\alpha-\beta} \sum_{j=0}^{\infty} \frac{\Gamma(\alpha+\beta+3)\,\Gamma(\beta+2j+2)(-A^2)^j}{(1+2j)!\,\Gamma(1+\beta)\,\Gamma(\alpha+\beta+2j+3)}$$

$$\times {}_2F_1\left(\begin{matrix}-1-2j,\ \alpha+1\\ -\beta-1-2j\end{matrix};-1\right) \tag{5·20}$$

Since in [8, p. 118] the value of approximate period has been compared with the exact period in case of sine non-linearity, which depends on ω_*^2 of [8, eq. 59, p. 118] the results (62), (66) and (67) remain the same due to the fact that there seems to be misprints in Garde's equations 54, 57 and 58 referred above.

It is interesting to observe that the approximate solution of the non-linear differential equations associated with generalized hypergeometric functions can be obtained in a similar manner and consequently the results given in this paper can be generalized. This will form the subject matter of a future communication.

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E fect of soil moisture conditions and potassium application on the chemical composition of the leaf of rice plant at different stages of growth and development

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Abstract

The chemical composition of the leaves of rice plant grown in different soil moisture conditions and treated with potassium indicated the following :

(1) Rice plant absorbs more nutrients during earlier than the later stages of growth.

(2) The concentration of nitrogen, silica and potassium was higher in moisture depleted than in liberally irrigated plants.

(3) No relation was found between the soil moisture and accumulation of phosporus, calcium and magnesium.

(4) The role of potassium upon the accumulation of different nutrients is not clear.

Introduction

For healthy growth and development of a plant at its different stages, it is very essential that not only the supply of various nutrients be adequate but also they should be in well balanced proportions. A study on the chemical composition of the plant carried out at different stages of growth can help to a great extent in understanding its nutritional requirement. Water being the carrier of different solutes right from the soil to different parts of the plant body, its status in the soil greatly affects the chemical composition of the tissues. Although potassium is a major plant nutrient and considerable knowledge with regard to its role in the plant has been acquired, not much information is available regarding its behaviour under the varying conditions of soil moisture.

The present investigation was undertaken with a view to find out the extent to which different soil moisture conditions and potassium application by different methods affect the chemical composition of rice plant at different stages of growth.

Experimental Method

A short duration variety of paddy namely, N_{22} was selected for the purpose. Other operations such as filling of pots with soil, raising of seedlings in the nursery, transplanting etc., remained the same as described in the authors' paper (1963).

Period of Growth

The observations started just after transplanting and continued till the end of advanced milking stage and covered the most active vegetative growth phases of the plant's life-cycle. *This part of life-cycle was divided into two periods of growth each of 30 days duration.* The first period represented the seedling to advanced tillering stage and the second included advanced tillering, flowering and advanced milking stages.

Arrangement of Pots

At the start of each respective period, the pots were taken inside the glass house to avoid the interference due to rain, dew, etc. The pots were then divided in two sets, the first received liberal but equal and measured volume of water, whereas in the second case, progressively depleted soil moisture conditions were created by stopping fresh supply of irrigation after allowing 2″ of standing water over the soil surface in the beginning. Pots under each set were arranged in a factorial experimental design.

Treatments

The normally irrigated plants of each of the periods were denoted by I_n, whereas the plants grown under the influence of depleted moisture conditions in the first and second periods were denoted by I_1 and I_2 respectively. Both types of plants, (normally irrigated and moisture depleted) in the two respective periods were treated with potassium in the form of potassium sulphate at the rate of 40 lb K_2O per acre in the following manners :

(1) K_0—Control *i.e.*, no application of potassium.

(2) K_1—The whole amount was applied in a single dose just after the commencement of the respective growth period.

(3) K_2—The whole amount was split in two equal doses, the first applied in the beginning and the other 15 days later.

(4) K_3—In this case, the amount was applied in three instalments at an interval of 10 days starting just after the commencement of each period.

All the treatment combinations falling under each period may be given as below :

Treatment number	First period	Second period
1	I_nK_0	I_nK_0
2	I_nK_1	I_nK_1
3	I_nK_2	I_nK_2
4	I_nK_3	I_nK_3
5	I_1K_0	I_2K_0
6	I_1K_1	I_2K_1
7	I_1K_2	I_2K_2
8	I_1K_3	I_2K_3

Sampling : Keeping in view the suggestions of Shear *et al* (1946). Hasegawa and Takaaki (1956) and others only fairly matured and functional leaf blades of middle portion of the plant were plucked at an interval of 10 days in each of the periods. However, plucking operation in both the sets *i.e*, moisture depleted

and normally irrigated conditions was done when more than 50 per cent plants in the former case were wilted. The wilting point was judged visually. The plucked leaves were at once dried in an electric oven at 110°C and were then ground in an electrically operated semi-micro grinding mill to a fine powder. The powder was again dried, filled in sampling bottles and sealed with wax.

Analytical Procedure : Total nitrogen was estimated according to the procedure recommended by Loomis and Shull (1938). The estimations of phosphorus, potassium, silica, calcium, and magnesium were done according to Piper (1950) and the method of wet digetion with sulphuric, nitric and perchloric acids as described in the procedure was followed. Phosphorus was estimated by the volumetric method.

Experimental Findings

A perusal of the accompanying Table indicates that except in a few cases, the concentration of all the nutrients falls as the plant ages. Taking the effect of irrigation on the concentration of different constituents, it may be noted that depletion of soil moisture reduces the nitrogen content in the early stage, but with the advancement of age, opposite trend is observed. Variation in the concentration of phosphorus due to irrigation is not appreciable. However, a critical examination points out that a slight withdrawal of soil moisture in the beginning of each period favours more accumulation of it, but it is lowered when the withdrawal is too much during the later stages of growth. Data pertaining to potassium content appears to be quite interesting. It illustrates very clearly that the depleted soil moisture condition favours more accumulation of it in the first period, but in the second period, the trend is entirely reversed, and it is the normal irrigation which encouraged it more. Withdrawal of soil moisture has also been found to encourage accumulation of higher amount of silica at all stages of growth and development. The extent to which irrigation is responsible for the calcium uptake is not clear. However, its concentration is markedly reduced when the moisture content of the soil approaches the wilting point. The role of irrigation on the magnesium content is also not clear from the data presented.

Further examination of the Table indicates that the application of potassium in general has got no effect on the accumulation of different nutrients. However, split application in case of moisture depleted plants, appears to encourage slightly more accumulation of nitrogen, phosphorus and potassium. On the other hand, concentration of silica, calcium and magnesium are not affected by its application in all the cases.

It is difficult to say any thing specifically regarding the combined effect of the soil moisture conditions and potassium application on the accumulation of various nutrients. However, split application of potassium and depleted soil moisture generally favour more accumulation of nitrogen and silica particularly during the later stages of growth and development.

Discussion

The experimental data presented in the Table point out that the nutritional requirement is very great during the earlier than the later stages of plant's growth. A number of workers have also obtained similar result. Gile and Carrero reported as early as 1915 that in case of upland rice, percentage of nitrogen, phosphorus, potassium and sulphur reduced with the advancement of plant's age. Burd (1919) and Russell (1961) have also expressed similar view. Rapid growth can only take place when there is an adequate quantity of enzymes present in the plant tissues.

These enzymes require an abundant supply of nutrients for their proper functioning. The growth is very rapid when the plant is young and this might have caused greater uptake of nutrients. On the other hand, the reduced absorption during the later stages might be due to the fact that a part of the requirement of the new developing area is generally met from the already accumulated nutrients in the matured leaves. It is also possible that during this part of the life-cycle, some of the unnecessary minerals are removed from the plant's body (Chapman, 1934, and thus the concentration of minerals is lowered. The removal of minerals generally takes place by shedding of dead and older matured leaves and also by excretions through the root system. Sayre (1948) have reported that total-amount of potassium in the aerial parts of maize plant decreases towards the end of growing season and this potassium is most probably excreted into the soil through the roots. The experimental results of the Central Rice Research Institute, Cuttack (Anonymous, 1961) have pointed out that after the application of nitrogenous fertilizer, the mineralised content of nitrogen in the soil decreases as the time phases and this might have also caused a reduced uptake of some nutrients in the older age.

With regard to the effect of different soil moisture conditions on the accumulation of various nutrients, it has been noted that reduced supply of soil moisture causes greater accumulation of nitrogen in the tissues of the plant. This result confirms similar findings of Miller and Duley (1925) and Emmert (1936). According to Richards and Wadleigh (1952), the less vegetative growth in the above case is most probably the main reason for its higher concentration. They are of the view that the rate of entry is approximately maintained in conjunction with the decreased rate of utilization in stunted plants growing under the influence of low availability of moisture, and this probably causes greater accumulation of various nutrients. On a similar ground, greater accumulation of silica at all stages and potassium during the first period is justified. It is not clear why depleted soil moisture condition forced a reduced accumulation of potassium during the second period of the growth. However, it is likely that due to reduced growth during this period, a very little amount is utilized in metabolic activities of the plant and greater portion of it is either excreted or not taken up by the root system. A slightly gre.ter content of phosphorus in case of partial withdrawal of soil moisture at the early stage of growth suggests that the supply of the nutrient is increased by more extension of root system, due to better aeration. On the other hand phosphorus, applied as a basal dressing in the beginning, might have been fixed in the soil very firmly later on and this might have led to less variation in absorption under different soil moisture conditions. A part from this, variable effects of soil moisture have also been found on the accumulation of calcium and magnesium and the result is more or less similar as reported by Maximov (1929), Thomas *et al* (1942 and 1943).

No information of any significance has been obtained with regard to the effect of potassium application by different methods on the accumulation of various nutrients. No proper explanation can be given on account of paucity of literature on this aspect.

Table Showing the Effect of Soil Moisture Condition and Potassium Application on the Average Chemical Composition (percentage of dry matter) of Leaf at Different Stages of Growth and Development

FIRST PERIOD

Treatments		Total nitrogen	Phosphorus (P_2O_5)	Potassium (K_2O)	Silica (SiO_2)	Calcium (CaO)	Magnesium (MgO)
				10 DAYS			
1	I_nK_0	4·84	1·14	3·06	10·53	0·62	0·33
2	I_nK_1	4·31	1·11	4·10	8·78	0·62	0·15
3	I_nK_2	4·75	1·29	3·91	9·36	0·67	0·29
4	I_nK_3	4·90	1·37	5·44	8·83	0·62	0 37
5	I_1K_0	3·89	1·26	5·97	13·78	0·67	0·38
6	I_1K_1	3·92	1·19	4·13	13·39	0·56	0·42
7	I_1K_2	3·99	1·32	4·68	13·03	0·62	0·36
8	I_1K_3	3·95	1·29	5·07	12·82	0·73	0·22
				20 DAYS			
1	I_nK_0	3·35	0·78	3·36	9·08	1·01	0·63
2	I_nK_1	3·19	0·75	3·98	8·20	1 06	0·78
3	I_nK_2	3·27	0·82	3·70	6·71	1·01	0·64
4	I_nK_3	3·31	0·81	3·52	6·21	1·12	0·53
5	I_1K_0	3·71	0·77	4·33	14·08	1·06	0·78
6	I_1K_1	3·84	0·69	4·44	13·93	1·01	0·83
7	I_1K_2	3·84	0·78	4·05	14·30	1·01	0·80
8	I_1K_3	3·85	0·72	4·03	13·25	0·90	0·78
				27 DAYS (WILTING POINT)			
1	I_nK_0	2·81	0·82	3·54	6·67	0·90	0·71
2	$I\ K_1$	2·65	0·71	3·63	7·90	1·01	0·31
3	I_nK_2	2·63	0·77	3·69	7·31	1·06	0·23
4	I_nK_3	2·63	0·68	3·77	10·28	0·95	0·42
5	I_1K_0	3·00	0·53	3·99	14·13	0·73	0·68
6	I_1K_1	3·03	0·59	3·95	15·04	1·01	0·38
7	I_1K_2	3·08	0 60	4·31	14·71	0·84	0·37
8	I_1K_3	3·09	0·55	4·10	15·26	0·62	0·45

SECOND PERIOD

40 DAYS

Treatments		Total nitrogen	Phosphorus (P_2O_5)	Potassium (K_2O)	Silica (SiO_2)	Calcium (CaO)	Magnesium (MgO)
1	I_nK_0	2·07	0·59	2·99	6·12	0·73	0·56
2	I_nK_1	2·14	0·70	2·88	6·25	0·67	0·38
3	I_nK_2	2·07	0·62	2·62	8·02	0·73	0·69
4	I_nK_3	2·00	0·68	2·46	6·52	0·73	0·65
5	I_2K_0	2·37	0·74	2·14	9·54	0·50	0·31
6	I_2K_1	2·63	0·73	2·26	9·98	1·06	0·39
7	I_2K_2	2·54	0·72	2·52	10·39	0·95	0·75
8	I_2K_3	2·09	0·84	2·22	7·96	1·01	0·75

(*Table Contd.*)

Treatments		Total nitrogen	Phosphorus (P_2O_5)	Potassium (K_2O)	Silica (SiO_2)	Calcium (CaO)	Magnesium (MgO)
				50 Days			
1	I_nK_0	2·16	0·61	2·63	8·26	0·84	0·52
2	I_nK_1	2·07	0·63	3·20	7·54	1·01	0·30
3	I_nK_2	2·57	0·67	2·08	9·57	0·73	0·49
4	I_nK_3	2·15	0·75	2·72	6·66	0·73	0·30
5	I_2K_0	2·39	0·57	2·33	9·78	0·78	0·43
6	I_2K_1	2·50	0·60	2·19	9·28	0·78	0·49
7	I_2K_2	2·54	0·61	2·10	9·33	0·67	0·36
8	I_2K_3	2·51	0·59	1·91	9·28	0·67	0·37
				54 Days (wilting point)			
1	I_nK_0	1·78	0·59	2·42	7·76	1·01	0·54
2	I_nK_1	1·55	0·64	2·87	7·13	1·12	0·27
3	I_nK_2	1·55	0·65	2·50	6·99	1·12	0·41
4	I_nK_3	1·76	0·69	1·41	7·18	0·90	0·45
5	I_2K_0	2·35	0·56	1·85	10·77	0·78	0·20
6	I_2K_1	2·28	0·56	1·93	11·21	0·67	0·17
7	I_2K_2	2·22	0·55	2·14	10·20	0·73	0·39
8	I_2K_3	1·96	0·52	2·21	10·29	0·73	0·15

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Synthesis of Halo Substituted Chalcones Part I

By

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Abstract

Observation by Geiger and Conn that Chalcone compounds possess marked antibacterial activity led us to prepare a number of 3-bromo-4-hydroxy-1-naphthyl styryl ketones from 3-bromo-4-hydroxy-1-acetonaphthone and aryl aldehydes by Claisen-Schmidt condensation. These compounds have been tested for their antibacterial properties and found to possess activities comparable to benzoic acid.

Introduction

In recent years a considerable amount of work has been done on the condensation of methyl aryl ketones with aromatic aldehydes to produce the so-called chalcones. These compounds and their bicyclic or polycyclic analogues[1] have been reported by a number of workers[2,3,4,5] to possess profound toxic[6,7] action against bacteria, fungus and also show anthelmintic, cardiovascular, etc. activities. This has tempted us to carry out studies in this direction. In the present communication synthesis of twenty-five compounds have been reported from 3-bromo-4-hydroxy-1-acetonaphthone with various aryl aldehydes in presence of alcoholic caustic potash solution. The synthesized compounds have been characterized by their C-H analyses (Table 1), tested for their antimicrobial activity by following the standard agar cup-plate method, compared against benzoic acid (Table 2).

The condensation of 3-bromo-4-hydroxy-1-acetonaphthone with different benzaldehydes in presence of concentrated caustic potash solution resulted into tarry masses giving a display of colours ranging from violet to dark brown and sometimes foul odoured products without giving the required compounds, whereas in presence of 15% alc.KOH beautiful crystalline compounds were deposited. This may be due to sensitivity of halogen substituted naphthols and hydroxy benzaldehydes towards the action of concentrated alkalis. Similar results were obtained during the condensation of 3-bromo-4-hydroxy-1-acetonaphthone and (2, 3 or 4)-nitro benzaldehydes even at this concentration of alkali solution. The products with methyl, methoxy and halo-substituted benzaldehydes were in quite good yield while those with hydroxy-benzaldehydes gave very poor yield. This is attributed to the resinification and/or side reactions of hydroxy benzaldehydes with alkali solution.

The antimicrobial activity of chalcone compounds is largely contributed by the bridging group -C=C-CO- as well as the substituents present in the either side rings. In the present study the compounds obtained by the interaction of 3-bromo-4-hydroxy-1-acetonaphthone and halo substituted benzaldehydes were

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most effective against the gram positive bacteria (*S. aureus*) as compared to those obtained with nitro, methyl, methoxy and hydroxy benzaldehydes. The marked antibacterial activity due to the presence of halogen atom in conjugation with the α, β-unsaturated ketonic group may be most probably due to the combined effect of the halogen atom and the extended conjugation, since halogen containing compounds are themselves highly antibacterial in nature. It has been found that the replacement of benzene nucleus by naphthlene in benzalacetophenone gave a slight augmentation in the toxic nature of these compounds.

TABLE I

Physical properties and analytical data of 3-Bromo-4 hydroxy-1-naphthyl-substituted styryl ketones

Substituents	Colour and shape of crystals	M. P. °C	Halochromism with con. H_2SO_4	Yield%	% Carbon Found	% Carbon Calc.	%hydrogen Found	%hydrogen Calc.
No substituent[a]	Colourless, needle	134	Yellowish red	74·0	64·81	64·59	3·59	3·68
3-methyl[b]	Light yellow, Prisms	133	Blood red	67·0	65·27	65·39	4·24	4·08
4-methyl[b]	Colourless, Rods	135	,,	70·5	65·30	65·39	4·31	4·08
2-Chloro[a]	,,	136	Greenish yellow	75·3	58·97	58·83	3·27	3·09
3-chloro[a]	White shining Needles	129	Yellowish red	69·6	58·75	58·83	2·83	3·09
4-Chloro[a]	Light yellow Rods	125–6	Blood red	77·0	58·69	58·83	3·15	3·09
2-hydroxy[b]	Silvery white Needles	132	Yellow	51·0	61·98	61·79	3·74	3 52
3-hydroxy[a]	,, prisms	133	Brown	54·5	61·83	61·79	3·41	3·52
4-hydroxy[b]	White, needles	131	Green	63·1	61·67	61·79	3·71	3·52
2 : 4-dihydroxy[c]	Cream colour Plates	134	Blood red	60·4	59·08	59·21	3·19	3·37
2-methoxy[c]	Silvery white plates	126	Blood red	75·6	62·83	62·66	3·73	3·91
3-methoxy[a]	Light yellow Rods	131	Greenish yellow	74·4	62·95	62·66	3·63	3·91
4 methoxy[a]	Light yellow Needles	134	Dull red	80·1	62·58	62·66	4·16	3·91
2 : 3-dimethoxy[a]	Light yellow plates	135	Green	82·1	60·87	61·01	4·36	4·11
3 : 4-dimethoxy[a]	Yellow, Plates	133	Greenish yellow	80·1	61·28	61·01	4·17	4·11

(*Table Contd.*)

Substituents	Colour and shape of crystals	M. P. °C	Halochromism with con. H_2SO_4	Yield %	% Carbon		% hydrogen	
					Found	Calc.	Found	Calc.
3 : 4-dimethoxy-6-nitro[b]	Golden yellow, Needles	109–10	Reddish orange	79·4	55·30	55·01	3·28	3·49
2-nitro[b]	Shining, Globules	132	Greenish yellow	61·0	57·47	57·28	3·27	3·01
3-nitro[a]	Colourless, Plates	120	,,	70·5	57·16	57·28	3·13	3·01
4-nitro[a]	Light yellow Rods	131	,,	75·5	57·19	57·28	3·31	3·01
4-hydroxy-[d] 3-methoxy	Cream colour Globules	130	Brown	64·0	60·43	60·15	3·56	3·75
5-bromo-[c] 4-hydroxy-3-methoxy	Cream colour, Globules	119	Violet	66·4	50·47	50·21	2·71	2·92
3 : 4-methylenedioxy-[c]	Light yellow, Plates	131	Dark red	80 1	60·71	60·45	3·14	3·27
5 : 6-Benzo-[a]2-Hydroxy	Light yellow, Rods	75	Reddish yellow	58·0	65·59	65·88	3·37	3·5
4 dimethyl[a] amino	Buff, Plates	118	Blood red	64·1	63·74	63·43	4·39	4·54
2-Furfuryl-[a] dene-3-bromo-4-hydroxy-1-acetonaphthone	Light, Plate yellow	110	Greenish yellow	59·3	59·51	59·47	3·19	3·21

a=EtOH, b=Aq. EtOH, c=AcOET d=EtOH–AcOEt.

Experimental

I. 3-Bromo-4-hydroxy-1-acetonaphthone :

The method of Akram[8] having failed, it was prepared by following the modified method. 10 g of 4-acetyl-1-naphthol[8] was dissolved in 150 ml of acetic acid and to this was gradually added 2·5 ml of bromine in 25 ml of acetic acid with stirring. It was kept for an overnight, poured into 500 ml of ice-cold water. The compound was collected, washed with water till free from acid, dried and crystallised from chloroform in the form of colourless needles, m.p. 134 (Found: Br, 30·1 $C_{12}H_9O_2$ Br required Br, 30·3%).

II. 3,4-Dimethoxy benzaldehyde[9] :

It was prepared by methylation of 3-methoxy-4-hydroxy benzaldehyde with dimethyl sulphate in alkaline solution.

III. 3-Bromo-4-hydroxy-1-naphthyl-2-chloro styryl ketone :

3-Bromo-4-hydroxy-1-acetonaphthone (0·01 mole) and 2-chloro benzaldehyde (0·01 mole) were dissolved in 30 ml of ethyl alcohol and to this was added 3 ml of 15% alcoholic caustic potash solution over a period of 20 minutes with constant stirring and allowed to stand at room temperature for 48 hours. The reaction mixture was diluted, acidified with 10% HCl, filtered and crystallised the crude compound in the form of colourless rods, m.p. 136°C. The remaining compounds of the series were prepared by adopting this method (Table 1).

The chalcones produce vivid colours when treated with concentrated sulphuric acid (Table 1).

The antimicrobial activity of these products was screened against *S. aureus* by following agar cup-plate method at $32 \pm 2°$ incubation temperature. Inoculum for the work were prepared from 24 hours old stationary culture and diameter of zones of inhibition were recorded in mm. (Table 2).

TABLE 2

The antimicrobial activity of 3-bromo-4-hydroxy-1-naphthyl substituted styryl ketones against *S. aureus*

Substituents	Conc. in mg/ml	Diam. of zone of inhibition in mm.
No substituent	24	13
3-methyl	22	12
4-methyl	23	12
2-chloro	20	14
3-chloro	19	15
4-chloro	21	14
2-hydroxy	27	–
3-hydroxy	26	–
4-hydroxy	28	–
2,4-dihydroxy	27	7
2-methoxy	24	7
3-methoxy	23	5
4-methoxy	22	5
2,3-dimethoxy	23	6
3,4-dimethoxy	24	6
3,4-dimethoxy-6-nitro	21	14
2-nitro	22	13
3-nitro	21	12
4-nitro	22	13
4-hydroxy-3-methoxy	26	–
5-bromo-4-hydroxy-3-methoxy	24	10
3,4-methylenedioxy	23	9
4-dimethylamino	22	10
Benzoic acid	20	12

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Syntheses of Some New 5' : 6'-Benzochalcone Analogues of Antimicrobial Importance Part VI

By

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Abstract

Four methyl naphthyl ketones, *i.e.*, 1-acetonaphthone, 4-hydroxy-1-acetonaphthone, 1-methoxy-4-acetonaphthone and 1-methoxy-2-acetonaphthone have been condensed separately with various aromatic aldehydes in presence of alcoholic caustic potash solution and characterized by their 2,4-dinitrophenylhydrazone derivatives. All the synthesized compounds showed halochromism with conc. sulphuric acid and hydroxy analogues (where hydroxyl group is in ketone part) gave distinct colour shades with alcoholic ferric chloride solution. These compounds have been tested against gram positive bacteria *S. aureus* and compared with benzoic acid.

Introduction

Chalcones as antibacterial agents against the gram positive organisms have been reported by Geiger and Conn[1] in 1945. These compounds and their derivatives also showed inhibitory action against, *S. hemolyticus*[2], *S. aureus*[3,4] *F. graminearum* and *B. alli.*[5] Wilson and Coworkers[6] observed that by the use of hydroxy and methoxy chalcones adrenaline was protected from destruction. Eaton and Davies[7] reported that out of all the compounds tested, those with two benzene nuclei connected by bridging grougs like, –CH=CH-CO– or –CH=CH–, were toxic to fruit-tree red spider mite. In an earlier communication[8] we have found that by replacing one of the two benzene nuclei with thiophenyl[8], furfuryl[9] and 8-hydroxy quinolinyl[9] groups and, of course, having different substituents in the second benzene nucleus, a remarkable change in the antimicrobial activities occur. With these facts, there seems to be every possibility that the conjugation of halogen atom[10], and/or amino group[11] with hydroxy and methoxy groups via a central conjugated system of double bonds,[1,12,13] of the type mentioned above, may result with higher degree of antimicrobial activities. By changing the position of halogen atom from ortho to meta, and then to para, we essentially increase the length of the central conjugated system which has halogen atom at its one end and hydroxy and/or methoxy group at the other. This inturn may, reinforce the antimicrobial activity of the compounds. Methoxy and hydroxy chalcones seems to have some toxic effect on higher animals,[7,14] but no study has been done on microbes.

In literature hardly any work has been reported about the antimicrobial activities of the naphthalene analogues of chalcone compounds and hence it was thought desirable to synthesize such compounds, supposing them to possess potential antimicrobial activities. We have achieved this by condensing 1-acetonaphthone, 1-hydroxy 4-acetonaphthone, 1-methoxy-4-acetonaphthone and 1-methoxy-2-acetonaphthone with various arylaldehydes in presence of alcoholic caustic potash solution at room temperature. The optimum preparative conditions were achieved and it was found that in presence of concentrated alkali

PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA OF 5′ : 6′-BENZOCHALCONES

			M. P. (°C)	% Yield	Halochromism with H_2SO_4	Molecular formula	% Found C	% Found H	% Calc. C	% Calc. H	D.N.P.'s M.P. (°C)	D.N.P.'s % N_2 Found	D.N.P.'s % N_2 Calc.	Conc. in mg./ml.	Diam. of Zone of inhib. in mm.
1.	2-Chloro-	Pale Yellow needles	87	63	Blood red	$C_{19}H_{13}OCl$	77·70	4·20	77·95	4·44	...	...	...	18	13
2.	4-Chloro-	Light yellow plates	223	66	Red	,,	77·78	4·60	77·95	4·44	...	..	...	18	12
3.	2-Hydroxy-	Yellow needles	145	23	Deep red	$C_{19}H_{14}O_2$	83·10	5·25	83·21	5·11	...	...	...	25	—
4.	4-Methoxy-	Yellow hexagonal plates	151	63	Orange red	$C_{20}H_{16}O_2$	88·15	5·80	88·33	5·55	...	...	...	21	6
5.	2-Chloro-1′-methoxy-	Yellow needles	154	87	Red	$C_{20}H_{15}O_2Cl$	74·25	4·55	74·42	4·65	245	10·90	11·14	19	12
6.	3-Chloro-1′ methoxy-	Pale yellow plates	141	79	Red	,,	74·27	4·49	74·42	4·65	232	10·88	11·14	18	13
7.	4--Chloro-1′ Methoxy-	Light yellow plates	126	89	Red	,,	74·54	4·59	74·42	4·65	242	11·25	11·14	17	12
8.	1'-Methoxy-	Yellow plates	97	75	Red	$C_{20}H_{16}O_2$	83·13	5·71	83·33	5·55	...	...	...	26	—
9.	1', 2-Dimethoxy-	Yellow plates	101	83	Blood red	$C_{21}H_{18}O_3$	78·97	5·36	79·24	5·66	229	11·00	11·24	25	6
10.	1',3-Dimethoxy-	Yellow plates	104	77	Blood red	,,	79·09	5·55	79·24	5·66	220	11·30	11·24	26	5
11.	1',4-Dimethoxy-	Light yellow plates	96	85	Blood red	,,	78·98	5·50	79·24	5·66	256	10·96	11·24	26	5
12.	2-Hydroxy-1′-methoxy-	Yellow plates	163	35	Red	$C_{20}H_{16}O_3$	79·00	5·11	78·94	5·26	244	11·30	11·57	27	—
13.	3-Hydroxy-1′-methoxy-	Green needles	165	50	Deep red	$C_{20}H_{16}O_3$	79·09	5·52	78·94	5·26	241	11·75	11·57	26	—
14.	4-Hydroxy-1′-methoxy-	Yellow needles	217	39	Blood red	,,	79·16	5·48	78·94	5·26	259	11·40	11·57	27	—
15.	5-Bromo-4-hydroxy-3,1′-dimethoxy-	Ochre yellow needles	117	58	Deep red	$C_{21}H_{17}O_4Br$	60·79	4·32	61·01	4·11	278·5	9·21	9·44	20	10
16.	4-Dimethoxyl-amino–1-'-methoxy-	Orange plates	137	71	Red	$C_{22}H_{21}O_2N$	79·64	6·41	79·75	6·34	230	13·48	13·70	19	5
17.	4-Chloro-4′-methoxy-	Yellow plates	126-127	84	Blood red	$C_{20}H_{15}O_2Cl$	74·20	4·40	74·41	4·65	...	...	...	19	7
18.	4,4'-Dimethoxy-	Yellow plates	97	82	Blood red	$C_{21}H_{18}O_3$	79·00	5·80	79·24	5·66	...	...	...	22	5
19.	3,4,4′ Trimethoxy-	Yellow hexagons	134	83	Reddish violet	$C_{22}H_{20}O_4$	75·58	5·92	75·86	5·74	...	...	...	25	—
20.	4′-methoxy-	Light yellow needles	80	78	Blood red	$C_{20}H_{16}O_2$	83·10	5·71	83·33	5·55	...	...	...	22	—

21.	4-Dimethoxyl-amino-4'-methoxy-	Orange plates	134-135	76	Blood red	$C_{22}H_{21}O_2N$	79·55	6·30	79·75	6·34	...	...	...	24	—
22.	3-Hydroxy-4'-methoxy-	Yellow hexagons	165	63	Red	$C_{20}H_{16}O_3$	79·10	5·30	78·94	5·26	...	...	...	25	—
23.	4-Nitro-4'-methoxy-	Golden yellow plates	214	84	Blood red	$C_{20}H_{15}O_4N$	72·50	4·25	72·72	4·54	...	...	...	—	—
24.	4-Methyl-4'-methoxy-	Yellow rods	108-109	87	Blood red	$C_{21}H_{18}O_2$	83·20	6·10	83·44	5·96	...	...	...	20	11
25.	2-Methoxy-4'-hydroxy	Yellow plates	182	72	Blood red	$C_{20}H_{16}O_3$	79·06	5·11	78·94	5·26	259	11·46	11·57	—	—
26.	3-Methoxy-4'-hydroxy-	Yellow plates	149	65	Blood red	,,	78·77	5·30	78·94	5·26	216	11·33	11·57	—	—
27.	4-Methoxy-4'-hydroxy-	Yellow rods	158	70	Blood red	,,	79·21	5·47	78·94	5·26	250	11·51	11·57	—	—
28.	2,4'-Dihydroxy-	Red rhombic crystals	198	28	Red	$C_{19}H_{14}O_3$	78·85	5·00	78·62	4·82	273	11·73	11·91	—	—
29.	3,4'-Dihydroxy-	Yellow plates	193	46	Red	,,	78·70	4·99	78·62	4·82	257	11·81	11·91	—	—
30.	4,4'-Dihydroxy-	Yellow needles	196	30	Orange	,,	78·38	4·98	78·62	4·82	258·5	12·20	11·91	—	—
31.	2,4,4'-Trihydroxy-	Buff-colored needles	194	31	Green	$C_{19}H_{14}O_4$	74·35	4·41	74·50	4·57	257	11·28	11·52	—	—
32.	2,4'-Dihydroxy-3-methoxy-	Yellow plates	195	51	Blood red	$C_{20}H_{16}O_4$	74·87	5·13	75·00	5·00	246	10·93	11·20	—	—
33.	4,4'-Dihydroxy-3-methoxy-5'-nitro-	Yellow needles	290	76	Green	$C_{20}H_{15}O_6N$	65·88	4·32	65·75	4·11	270	12·56	12·84	20	13
34.	4,4'-Dihydroxy-3-methoxy-	Yellow needles	197	37	Red	$C_{20}H_{16}O_4$	75·23	4·82	75·00	5·00	262	11·02	11·20	—	—
35.	5-Bromo-4,4'-Dihydroxy-3-methoxy-	Cream-colored needles	195	51	Red	$C_{20}H_{15}O_4Br$	60·00	3·50	60·15	3·76	253	9·41	9·69	19	11
36.	6-Bromo-4,4'-Dihydroxy-3-methoxy-2-nitro-	Yellow plates	174	70	Green	$C_{20}H_{14}O_6NBr$	53·80	3·00	54·05	3·15	246	10·89	11·21	20	13
37.	2,3-Dimethoxy-4'-hydroxy-	Yellow plates	222	74	Blood red	$C_{21}H_{18}O_4$	75·31	5·51	75·44	5·39	235	10·70	10·89	25	5
38.	3,4-Dimethoxy-4'-hydroxy-	Yellow plates	93	71	Red	,,	75·19	5·23	75·44	5·39	271	10·75	10·89	22	
39.	3 : 4-Methylene-dioxy-4'-hydroxy-	Yellow cylinders	163	76	Violet	$C_{20}H_{14}O_4$	75·62	4·45	75·43	4·40	...	...	...	25	4
40.	2,4'-Dihydroxy-5:6–dibenzo	Pale yellow	83	35	Green	$C_{23}H_{16}O_3$	80·89	4·92	81·17	4·70	292	10·54	10·76	23	5
41.	4-Dimethyl-amino-4'-hydroxy-	Yellow needles	196	60	Red-Orange	$C_{21}H_{19}O_2N$	79·29	6·10	79·50	6·00	261	13·78	14·08	20	5
	Benzoic acid		—	—	—	—	—	—	—	—	—	—	—	20	12

solution and higher temperature dark brown tarry masses of unknown composition were formed. From this, no crystalline compound could be obtained.

The chalcone analogues of these series have been characterized by their 2,4-dinitrophenylhydrazones. All these compounds showed halochromism when dissolved in conc. sulfuric acid (Table 1), compounds from No. 25-41, which have hydroxyl groups in the ketone part, responded to alcoholic ferric chloride test, producing distinct green colour shades, except that compound Nos. 31, 33, 36 and 40, which gave reddish violet, red, brownish red and violet color shades respectively.

The antimicrobial activity of these compounds were screened against *S. aureus* by following standard agar-cup-plate method, and compared with benzoic acid. The inoculum for the test were prepared from 24 hours old stationary culture and diameter of zones of inhibition were measured in mm. at ($37 \pm 2°$) incubation temperature (Table 1).

Experimental

1-Hydroxy-4-acetonaphthone :[15] It was prepared by the action of acetyl chloride (24 g) on 1-naphthol (40 g) using anhydrous zinc chloride (40 g) as a catalyst and nitrobenzene (200 ml) as solvent.

1-Methoxy-4-acetonaphthone :[15] It was prepared by the action of dimethyl sulfate on 1-hydroxy-4-acetonaphthone.

1-Methoxy-2-acetonaphthone :[16,17] 1-Naphthol was methylated by usual method to give 1-naphtholmethyl ether, which was then reacted with acetic anhydride using anhydrous aluminium chloride in carbon disulfide and collected at 181-2/4 mm.

5′ : 6′-Benzochalcones : The chalcone analogues of this series were prepered by our general procedure which has already been described in our earlier publications.[9,18,19]

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Effect of soil moisture conditions and Gibberellin application on the chemical composition of leaves of rice plant at different stages of growth and development

By

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Abstract

Various concentrations of gibberellin were sprayed on rice plants grown under different soil moisture conditions. The study on chemical composition of the leaves indicated the following :

(1) Soil moisture and not the gibberellin largely influences the accumulation of nutrients.

(2) Gibberellin application may favour accumulation of salts when irrigated liberally.

Introduction

Amongst the various factors which control the movement of different nutrients from particle to particle of soil and also from soil to plant, water plays the most dominant role. It acts as a carrier of nutrients from soil to various organs of the plant and hence chemical composition of a plant largely depends upon the status of the soil moisture.

Gibberellin, which is a plant growth regulator, has been known to cause varying degree of vegetative growth and early flowering in different type of plants (Brian and Grove, 1957). A study which may help in understanding the effect of its application on the relative concentration of various nutrients under the influence of different soil moisture conditions appears to be quite useful. It is hoped that this work, which intends to reveal the chemical composition of leaves at different stages of growth, will not only throw light on the nutritional requirement of the plant but also its irrigational need. So far as is known, no such work appears to have been reported in literature.

Experimental Method

The study was conducted on a mid-duration variety of paddy, *viz*, T_{21}. Other preliminary operations such as raising of seedlings in the nursery, filing of the pots with soil, puddling, transplanting, application, of insecticide, etc., remained the same as mentioned in the authors' paper (1963).

Periods of Growth : The observations started just after transplanting and continued till the end of advance milking stage and covered the most active vegetative growth phases of the plants life-cycle. This part of the life-cycle was divided into two periods of growth each of 45 days duration. The first period represented the seedling and advance tillering stages and the second included advance tillering, flowering and advance milking stages. Till the commencement

of respective growth period, plants were irrigated liberally with equal and measured volume of water.

Arrangement of Pots : At the start of each respective period, the pots were taken inside the glass-house to avoid the interference due to rain, dew etc. The pots were then divided in two sets. The first received liberal but equal and measured volume of water, whereas in the case of the second, progressively depleted soil moisture conditions were created by stopping fresh supply of irrigation after allowing 2″ of standing water over the soil surface in the beginning. The pots under each set were arranged in a factorial experimental design.

Treatments : The normally irrigated plants of each of the periods were denoted by I_n, whereas the plants grown under the influence of depleted moisture conditions in the first and second periods were denoted by I_1 and I_2 respectively. Irrepective of the soil moisture conditions, following concentrations of gibberellin were sprayed over plants at an interval of 15 days starting just after the transplanting and were continued till the beginning of the milking stage.

(1) G_0 - Control, *i.e.*, no application of the hormone.

(2) G_1 - 25 p.p.m.

(3) G_2 - 50 p.p.m.

(4) G_3 - 100 p.p.m.

All treatment combinations falling under each period may be given as below :

Treatment No.	Period I	Period II
1	I_nG_0	I_nG_0
2	I_nG_1	I_nG_1
3	I_nG_2	I_nG_2
4	I_nG_3	I_nG_3
5	I_1G_0	I_2G_0
6	I_1G_1	I_2G_1
7	I_1G_2	I_2G_2
8	I_1G_3	I_2G_3

Sampling : Keeping in view the suggestions of Shear *et al* (1946), Hasegawa and Takaaki (1956) and others, only fairly matured and functional leaf blades of middle portion of the plant were plucked at an interval of 10 days in each of the periods. However, plucking operation in both the sets *i.e.*, moisture depleted and normally irrigated conditions was done when more than 50 per cent plants in the former case were wilted. The wilting point was judged visually. The plucked leaves were at once dried in an electric oven at 110°C and were then ground in an electrically operated semi-micro grinding mill to a fine powder. The powder was again dried, filled in sampling bottles and sealed with wax.

Analytical Procedure : Total nitrogen was estimated according to the procedure recommended by Loomis and Shull (1938). The estimations of phosphorus, potassium, silica, calcium and magnesium were done according to Piper (1950) and wet digestion method (sulphuric + nitric + perchloric acids) was employed. Phosphorus was estimated by the volumetric method.

Experimental Findings

A critical study of the accompanying Table manifests the dominating nature of the soil moisture upon the accumulatian of various nutrients by the plant. It is apparent that in a late maturing variety of paddy, nitrogen content is generally lowered with the advancing age till it approaches more or less a constant value. It has also been noted that except in the beginning of the first period, accomulation is generally more favoured by depleted soil moisture than the normally irrigated condition. In case of phosphorus, soil moisture has been found to affect only in the earlier part of the life-cycle. It has been observed that normal irrigation causes more concentration in the beginning, then it is lowered for sometime and in the later stages of growth more or less an uniform value is obtained. On the other hand, moisture depleted plants accumulate less amount in the beginning, then the efficiency is increased considerably for sometime, but in the later stages it is not much affected. Except in few cases, potassium content has always been found greater in moisture depleted plants than the normally irrigated ones. Similar trend has also been noted in silica concentration. It may be seen that lowering of soil moisture at the start of each period encourages greater accumulation of calcium and later on the concentration is reduced. With regard to magnesium, variable results have been obtained. In general, depleted soil moisture condition slightly favours more accumulation.

Taking the effect of gibberellin it may be pointed out that it has practically failed to influence the accumulation of different constituents. However, in a number of cases lower concentrations, particularly 25 p.p.m. have given better results than the higher concentrations.

Discussion

In the present investigation, soil moisture has very clearly played the most dominent role in controlling the nutrient accumulation. Except in a few cases, withdrawal of soil moisture encourages more concentration of different nutrients such as nitrogen, phosphorus, potassium, silica, calcium and to some extent magnesium also. It appears that a low availability of moisture causes stunting in growth and thereby greater concentration of nutrients per unit of dry matter results. Richards and Wadleigh (1952) were of the same opinion. They have stated that the rate of entry is approximately maintained in conjunction with the decreased rate of utilization in the shunted plants growing under the influence of low availability of moisture, and this probably causes greater accumulation of many of the nutrients. The shunting in growth may be due to non-functioning of some vital enzymes under the low supply of moisture. Burd (1919) and Russell (1961) have also stated that for rapid growth, functioning of different enzymes is most essential. A progressive low concentration of different nutrients with the advancing age in a number of cases might be due to the fact that a part of the requirement of the new developing area at later stages is generally met from the already accumulated nutrients in the matured leaves. It is also likely that during this part of the life cycle, some of the unnecessary minerals are removed from the plants body (Chapman, 1934). The removal of minerals generally takes place by shedding of dead and older matured leaves and also by excretion through the root system (Sayre, 1948).

Table Showing the Influence of Soil Moisture Conditions and Gibberellin Application on the Average Chemical Composition (percentage of dry matter) of Leaf at Different Stages of Growth and Development

Treatments	Total nitrogen	Phosphorus (P_2O_5)	Potassium (K_2O)	Silica (SiO_2)	Calcium (CaO)	Magnesium (MgO)
I PERIOD						
15 DAYS						
1. I_nG_0	4·11	0·82	3·69	7·37	0·73	0·36
2. I_nG_1	4·18	0·82	4·03	7·78	0·73	0·40
3. I_nG_2	3·61	0·85	3·40	7·83	0·73	0·29
4. I_nG_3	3·16	0·84	3·99	7·77	1·01	0·31
5. I_1G_0	3·77	0·63	4·95	12·55	1·12	0·96
6. I_1G_1	2·35	0·63	4·62	11·46	1·34	0·84
7. I_1G_2	3·16	0·66	4·86	12·36	1·23	0·80
8. I_1G_3	3·23	0·64	4·40	11·06	1·29	0·85
30 DAYS						
1. I_nG_0	2·27	0·72	3·79	6·71	0·67	0·49
2. I_nG_1	2·35	0·75	5·05	7·50	0·56	0·50
3. I_nG_2	2·49	0·74	4·29	6·92	0·62	0·36
4. I_nG_3	2·52	0·84	3·43	7·44	0·84	0·67
5. I_1G_0	3·36	0·82	4·89	11·36	0·73	0·86
6. I_1G_1	3·50	0·78	4·48	11·58	0·73	0·91
7. I_1G_2	2·94	0·74	5·29	13·82	1·23	0·96
8. I_1G_3	2·74	0·75	4·54	12·25	0·78	0·89
40 DAYS (WILTIHG POINT)						
1. I_nG_0	2·50	0·64	1·63	7·40	1·01	0·47
2. I_nG_1	2·37	0·53	2·62	7·18	1·01	0·37
3. I_nG_2	2·60	0·53	2·91	7·64	0·90	0·31
4. I_nG_3	2·72	0·58	3·23	7·16	0·95	0·45
5. I_1G_0	2·65	0·72	5·22	8·60	0·56	0·29
6. I_1G_1	2·53	0·74	6·97	8·12	0·70	0·65
7. I_1G_2	2·61	0·74	6·62	9·15	0·70	0·62
8. I_1G_3	2·63	0·80	5·19	6·28	0·84	0·62
II PERIOD						
60 DAYS						
1. I_nG_0	1·68	0·49	1·84	7·58	1·06	0·38
2. I_nG_1	1·27	0·74	4·45	7·94	0·73	0·30
3. I_nG_2	1·60	0·61	2·26	9·30	1·12	0·15
4 I_nG_3	1·68	0·66	2·08	6·92	0·93	0·11
5. I_2G_0	1·74	0·49	2·33	9·11	1·01	0·37
6. I_2G_1	1·81	0·48	2·53	9·21	0·73	0·16
7. I_2G_2	1·72	0·52	1·28	9·26	1·12	0·30
8. I_2G_3	1·63	0·47	1·50	6·94	0·90	0·13

(Table Contd.)

Treatments	Total nitrogen	Phosphorus (P_2O_5)	Patassium (K_2O)	Silica (SiO_2)	Calcium (CaO)	Magnesium (MgO)
			75 DAYS			
1. I_nG_0	1·44	0·17	3·66	6·14	0·78	0·33
2. I_nG_1	1 87	0·47	2·96	7·00	0·84	0·69
3. I_nG_2	1·58	0·46	3·97	6·07	0·73	0·35
4. I_nG_3	1·76	0·43	5·84	5 99	0·78	0·54
5. I_2G_0	1·86	0·47	4·40	7·00	0·73	0·44
6. I_2G_1	1·98	0·52	5·39	8·39	0 73	0·56
7. I_2G_2	1·88	0·52	3·81	7·95	0·67	0·49
8. I_2G_3	1·77	0·44	3·50	6·66	0·45	0·62
			80 DAYS (WILTING POINT)			
1. I_nG_0	1·81	0·53	3·03	7·07	0·34	0·44
2. I_nG_1	1·74	0·45	2·61	7·15	1·01	0·49
3. I_nG_2	1·74	0·51	3·52	6·53	1·12	0·42
4. I_nG_3	2·00	0·59	3·99	6·53	1·12	0·56
5. I_2G_0	2·02	0·52	3·16	8·16	1·06	0·58
6. I_2G_1	2·17	0·50	5·16	8·26	0·67	0·65
7. I_2G_2	2·07	0·51	4·82	8·43	0·73	0·59
8. I_2G_3	2·15	0·45	4·15	8·07	0·39	0·42

The role of gibberellin on the concentration of different constituents is not clear. However, application of a higher concentration of it, has lowered the content of different nutrients in a number of cases. This might be due to a greater vegetative growth with the result the concentration of different nutrients per unit weight of the dry matter is lowered. Thakur and Negi (1959) also observed that in case of nitrogen, gibberellin application causes lowering of its concentration in sugarcane plant.

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Adsorption of Glycine on Activated Sugar Charcoal

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The present communication deals with the sorption of amino-acetic acid at 17°C by sugar charcoal activated at 220°C and verification of Freundlich Relationship. The values of constants so obtained are $K = 1 \cdot 99 \times 10^2$ and $1/N = 1 \cdot 10$.

Experimental

Preparation of Sugar charcoal : It has been prepared in accordance with the method used by Jain and Jha (Journal of Indian Chemical Society Vol. XVII No. 11, 1940 Page 685).

Method of Analysis : The adsorption experiments were carried out by weighing exactly 1 gm of sugar charcoal in clean dry glass bottles of similar size to which 50 ml. of glycine solution of different concentrations (in ppm) were added. The bottles were shaken for same length of time and kept for 12 hours after which the amount of solute was determined in supernatant liquid by using Sorsenson formalin titration method. The amount of material adsorbed was calculated from initial and final concentrations.

The results are tabulated as follows :

TABLE

Sl. No.	Conc. of glycine Before sorption (ppm) C_0	After sorption (ppm) C_e	Amount adsorbed x (ppm)	x/m	Log_{10} x/m	Log_{10} C_e
1	100×10^3	88×10^3	12×10^3	12×10^3	4·0792	4·9445
2	80×10^3	70×10^3	10×10^3	10×10^3	4·000	4·8451
3	60×10^3	$53 2 \times 10^3$	$6·8 \times 10^3$	$6·8 \times 10^3$	3·8325	4·7243
4	50×10^3	$45·2 \times 10^3$	$4·8 \times 10^3$	$4·8 \times 10^3$	3·6812	4·6551
5	40×10^3	$36·8 \times 10^3$	$3·2 \times 10^3$	$3·2 \times 10^3$	3·5050	4·5658
6	20×10^3	18×10^3	2×10^3	2×10^3	3·3010	4·2554

Curve II shows the variation of x/m and C_e (equilibrium conc.) where as curve I is a plot of log x/m (Total amount adsorbed) and Log C_e (equilibrium conc)

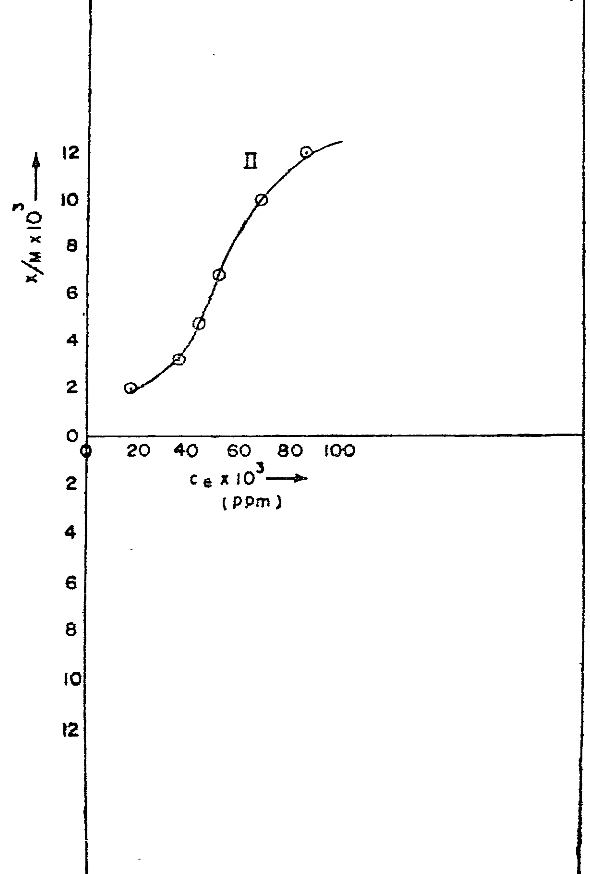
The classical adsorption isotherm is

$x/m = K\ Ce^{1/N}$ where N is an arbitrary parameter chosen to fit the data.

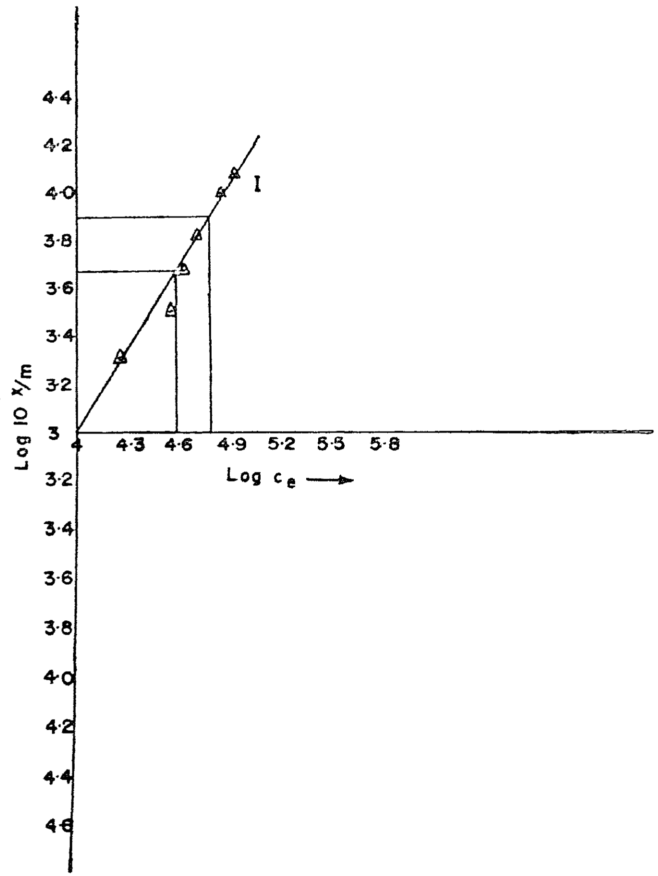
or $\text{Log } x/m = \text{Log } K + I/N \text{ Log } C_e$—(A)

According to equation A curve I should be a straight line and this is in agreement with the experimental values.

A GRAPH BETWEEN x/m AND c_e



A GRAPH BETWEEN LOG x/m AND LOG10 c_e



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Changes in nutrient content of soils caused by growing wheat and rice in rotation under pot-culture conditions

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Introduction

With regard to the complexity of their forms, the major plant nutrient elements can be listed in the order, Nitrogen, Phosphate and Potash. More than 90% of the soil nitrogen is in organic forms and in tropical mineral soils the content of organic phosphate and potash is very little.

In inorganic forms nitrogen exists in the soil as NO^{-}_{3} and NH^{+}_{4} ions in solution, exchangeable NH^{+}_{4} and fixed ammonium. The major part of the organic N is proteinaceous in nature. The presence of considerable amounts of amino acids and amino sugars in acid hydrolysates of soils has been reported by Bremner (1965*a*). Of less quantitative importance are the purine and Pyrimidine derivatives However, the fractionation and identification of organic forms of N poses so great a puzzle that even now about 45–70% of nitrogen remains to be accounted for its nature.

The phosphate in the soil is in the main in combination with Ca, Al, Fe and Mn. There are different compounds encountered in combinatian with each of these cations and they have a wide range in their solubility and crystallinity. As a result of fixation in the soil and its relatively immobile character, phosphate tends to accumulate in the different inorganic forms after repeated phosphatic fertilization.

Excluding potassium in soil organisms, the total K in soil may be classified as (1) Water soluble K, Ks (2) Exchangeable or adsorbed K, Ke (3) Fixed or difficulty exchangeable K, Kf and (4) Lattice or non-exchangeable K, Kl (Wiklander, 1954). The relationship between the first three forms which are of importance in the immediate K supply to the plant, may be represented as,

$$\text{Water Soluble K} \underset{\text{Very rapid}}{\overset{\text{Very rapid}}{\rightleftarrows}} \text{Exchangeable K} \underset{\text{Very slow}}{\overset{\text{Relatively rapid}}{\rightleftarrows}} \text{Fixed K}$$

The above mentioned forms of each of these nutrients are in dynamic equilibrium with one another. Their equilibria are constantly disturbed by the growing plant and by physical or chemical or biochemical changes in the soil body. In as much as the behaviour of the nutrient element is influenced by the forms of it taking part in the hetorogenous equilibria, an understanding of the distribution of the forms of native nutrient and the reaction products of applied

nutrient is of considerable importance in profitable and efficient crop nutrition. Chemical fractionation studies of the nutrient elements is of great value in tracing such changes in their forms. An attempted study in characterising the changes in the levels of some forms of N, P and K and some available trace elements in soils caused by growing wheat, (*Triticum aestivum*) and rice (*Oryza sativa*) in rotation under pot-culture conditions is discussed in this paper.

Experimental

(1) *Pot-culture experiments* :

Non-acid alluvial soils from 18 localities of Delhi State belonging to the Gheora and Mehroili soil series were used in this study. About 4·5 Kg. of fine earth was taken in each earthern pot. There were five treatments namely, control, NP, PK, NK and NPK. The elements were added at one level namely 80 Kg/ha for N, 60 Kg/ha for P_2O_5 and 30 Kg/ha for K_2O using solutions of urea, super phosphate and potassium chloride respectively. Each treatment was replicated four times and a completely randomised design was adopted. All the pots received trace elements at the rate of 0·62 Kg/ha of Boric acid and 1·24 Kg/ha of sulphate of Manganese, Zinc and Copper. The treatment structure was common to each of the four crops studied in rotation. No provision was made for free leaching of solution from the Pots. The crops were grown to maturity. During rabi 1967–68 (Nov.-April) wheat, variety, sonalika was used as the test crop. The post-harvest soil samples from all the pots of a single soil were pooled together and this potted soil was used again for the second test crop of rice, variety, IR-8, during kharif, 1968 (August–December). After completion of the experiment, these potted soils were used to raise a third crop of wheat, variety, sharbati Sonora, during rabi 1968–69 (Nov.–April) and the experiment was concluded after the fourth crop of rice, variety, padma during kharif, 1969.

(2) *Soil Analysis*

Since sequential fractionation procedures were adopted for following the changes in the distribution of the forms of N, P and K, the details of the procedure are given below. A composite soil sample from all the pots (control and treated) of all the localities was used for analysis. Duplicate fractionations and determinations of N, P and K were performed on each soil sample.

(*i*) *Fractionation of Nitrogen* : The forms considered of importance in short-term cropping were (1) Exchangeable NH^+_4 + NO^-_3 (2) Fixed NH^+_4 (3) Total hydrolyzable N (4) hydrolyzed NH^+_4 (5) Hexosamine and (6) Amino acid N. Hence, a flow-sheet combining the procedure given by Cheng and Kurtz (1963) and Keeny and Bremner (1964) was adopted. The nitrogen in each of the above forms was determined by macro-Kjeldahl digestion and distillation as described by Bremner (1965*b*).

A 20 g. of soil (< 2mm) was leached with 100 ml. of N.KCl (pH 1) and exchangeable NH^+_4 + NO^-_3 + N were determined together in the leachate by alkaline distillation with Devarda's alloy. The soil residue was digested at 100°C under reflux for 12 hours with 80 ml of 6 N.HCl, filtered through No. 50 filter paper and the residue washed with water. The hydrolyzate was adjusted to pH 6·5 ± 0·1 electrometrically with ION.NaOH and the neutralised hydrolyzate was made upto 250 ml volume. The hydrolyzable N was determined by digesting a portion of the hydrolyzate with Conc. H_2SO_4, K_2SO_4 – Catalyst mixture and distilling the digestate with ION.NaOH. Hydrolyzed NH^+_4 – N was determined by distillation with MgO. Ammonium + Hexosamine-N was determined by distillation with phosphate-borate buffer (pH 11·2). Amino acid N was determined

by steam distillation with phosphate borate-buffer (pH 11·2) and 5N.NaOH after treatments with 0·5N.NaOH (100°C) to decompose hexosamines and remove ammonium and with citric acid and Ninhydrin (100°C) to convert α-amino N to ammonium-N. The total soil N was determined by the salicylic acid method modified to include treatment with water (Bremner, 1965*b*). The unidentified forms of organic N, non-hydrolyzable N and hexosamine N were calculated by difference.

Available N was determined by the organic C method and alkaline $KMnO_4$ method (Muhr *et al.* 1965).

(*ii*) *Fractionation of Phosphate*: The procedure adopted was essentially the same as proposed by Chang and Jackson (1957) with modifications as recommended by Khin and Leeper (1960). A 0·5. g. soil (< 0·5 mm) was successively extracted with $N.NH_4Cl$, 0·5 $N.NH_4F$ (pH 8·5), 0·IN. NaOH and 0·5 $N.H_2SO_4$ to give saloid-P, Al-P, Fe-P and Ca-P. A separate soil sample was used to determine the occluded forms of P after removing the organic P by ignition of the soil at 450°C for 1 hour and subsequent extraction with 0·IN. NaOH, 0·5 $N.H_2SO_4$, Sodium Citrate-bicarbonate-dithionite (occluded Fe-P) and 0·1 N. NaOH (occluded Fe-Al-P). The phosphate in the extracts was determined colorimetrically by the molybdenum blue colour method using a Klett-Summerson colorimeter.

Available phosphate was determined by Olsen's method and Bray-I method as described by Muhr *et al.* (1965).

(*iii*) *Fractionation of Potassium*: A 10·g soil (< 0·5 mm) was shaken with 50 ml. of water for 1 hour and filtered through No. 50 filter paper using a Buchner funnel (water soluble K). The soil residue was leached intermittantly with neutral $N.NH_4OAC$ through No. 1 filter paper and made up to 250 ml (exchangeable K). The soil residue was boiled with 100 ml of $N.HNO_3$ for 10 minutes and leached with 0·2N. HNO_3 through No. 1 filter paper to get 250 ml. volume (Fixed K, Rouse and Bertramson, 1949). Potassium in the extracts was analysed using a systronix flame photometer.

(*iv*) *Trace elements*: The procedures described by Chapman and Pratt (1961) were followed to determine the available Cu, Zn and Mn. Available Cu was determined by the Carbamate method using 0·1 N HCl as the extractant, available ZN as the dithiozone-carbamate complex using $N.NH_4OAC$ as the Extractant and available Mn by the Periodate method using 3 N. Ammonium Phosphate as the extractant.

Results and Discussion

Crop plants differ in their ability to utilise different forms of the major plant nutrients. Such differences become more marked when relatively immobile forms of nutrients such as phosphate or fixed K are considered or when two crops like wheat and rice having contrasting types of soil-root environment are considered. In general the differences in the feeding power for the diverse forms of nutrient exhibited by crops are due to their differences in root habit and in exchange property of the absorbing root surface In the present study the soil in the pots for the wheat crop was kept under field-moist condition while for the rice crop it was kept under waterlogged condition. Certain important observations on the changes in the distribution of forms of major nutrients caused by wheat and rice grown in rotation under contrasting soil water regimes are discussed below.

The changes in the distribution of forms of N are presented in Table 1. Appreciable decrease in total N, available N and exchangeable $NH^+_4 + NO^-_3$ - N occurred after rice. Out of these, however, much significance cannot be attached to the decrease in exchangeable $NH^+_4 + NO^-_3$ - N because they depend so much on the time of sampling and the pre-treatment of the sample prior to analysis. The fixed NH^+_4 remained unaltered after the growth of the four crops. In each sample not more than 10% of the total N could be accounted for in the inorganic forms signifying the predominantly organic nature of soil N and the importance of its transformation to meet the N needs of the growing plant. Cheng and Kurtz (1963) observed that over 90% of added N in soils was found in the hydrolytic products of soil organic matter mainly as amino acid N, amino sugar N and hydrolyzed NH^+_4.

The total hydrolyzable N increased after the first wheat crop, changed very little after rice and decreased after the third wheat crop. A complementary pattern was reflected in the status of non-hydrolyzable N (Acid insoluble humin N). Thus this fraction decreased progressively except after the third wheat crop.

TABLE 1

Effect of crop rotation on forms of soil N

N content (Mg N/100 g. Air dry soil)

Forms of N	(1) Uncropped Soil		(2) After Wheat 1967–68		(3) After Rice 1968		(4) After Wheat 1968-69		(5) After rice 1969
(1) Total N	60·6	=	60·9	-	50·5	=	53·0	-	43·8
(2) Exch. $NH^+_4 + NO^-_3$N	2·9	=	2·6	-	1·3	=	1·4	=	0·9
(3) Fixed NH^+_4	3·2	=	3·0	=	3·0	=	2·9	=	3·1
(4) **Total hydrolyzable N**	36·7	+	45·1	=	42·4	-	35·1	=	33·7
(a) Ammonium	5·9	=	5·2	=	5·4	=	5·6	=	5·9
(b) Hexosamine	4·2	=	4·1	-	3·0	-	2·3	=	2·1
(c) Amino acid	8·3	-	6·1	+	9·2	-	6·6	+	9·8
(d) Unidentified forms (acid insoluble humin N)	18·3	+	29·7	-	24·8	-	20·9	-	15·9
(5) **Non hydrolyzable N** (acid insoluble humin N)	17 8	-	10·2	-	3·8	+	13·3	-	6·1
(6) **Available N by**									
(a) Organic carbon %	0·478	+	0·516	-	0·476	-	0·452	-	0·413
(b) Alkaline Permanganate method–Kg/he	231	-	219	-	204	-	193	-	184

Among the different forms of hydrolyzable N, there was no change in the hydrolyzed NH^+_4 fraction and a decline in hexosamine fraction was noticed after the second rice crop. It is interesting that amino acid N decreased after the first and third wheat crop but increased after the second and fourth rice crop. The unidentified forms of the hydrolyzable N (Probably acid soluble humin N) increased after the first wheat crop and progressively decreased thereafter. The relative change in the different organic forms within the total hydrolyzable N after each crop was in accord with the net change of this particular fraction. Keeney and Bremner (1964) showed that the loss of any particular organie N fraction on cultivation was roughly proportional to the amount present before cultivation.

The changes in the distribution of the inorganic forms of phosphate are given in Table-2. Compared to the uncropped soil there has been an increase in the total inorganic P (as obtained by sum of P fractions) of the soil at the end of the fourth crop. This increase is due to the fixation of applied phosphate and accumulation in the 'active' fractions and to the low percent utilisation of soil P by crops. The 'inactive' occluded forms of phosphate have remained unaltered.

TABLE 2

Effect of crop rotation on forms of soil phosphorus

(Forms of P. ppm. Air dry soil)

Particulars	Saloid-P 1	Al-P 2	Fe-P 3	Ca-P 4	OCC Fe-P 5	OCC Fe-Al-P 6	Sum 1-6	Av.P in Kg/ha Olsen	Bray I
(1) Uncropped soil	17	44	37	347	26	8	(489)	18·7	72·0
	+	+	-	+	=	=		-	+
(2) After wheat 1967-68	22	54	28	365	35	8	(512)	16·4	108·0
	-	=	+	=	=	=		+	-
(3) After rice 1968	4	54	42	365	38	7	(510)	23·0	94·0
	+	-	+	+	=	=		-	=
(4) After wheat 1969-69	13	47	52	391	34	8	(545)	18·8	91·8
	-	=	+	+	=	=		+	-
(5) After rice 1969	Traces	45	61	411	36	10	(563)	25·8	79·2

After the first wheat crop the saloid P, Al-P and Ca-P have increased and the Fe-P decreased. After the third wheat crop, saloid P, Fe P and Ca-P increased and Al-P decreased. On the other hand, after the second and fourth rice crop, Fe-P increased and saloid P decreased with little change in Al-P. Thus the different P fractions are tapped effectively and in a complementary fashion by wheat and rice grown in rotation. The ability of rice to utilise Fe-P which has a very low solubility product has special significance in crop rotation. Islam and Elahi (1954) demonstrated the reduction of Fe^{3+} to Fe^{2+} under water-logged conditions and its relation to available P. The process of reduction and increased availability of P was greatly enhanced by the addition of oxidizable materials like green manure. Rodrigo (1966) considered Fe-P to be the main source of soil P for low-land rice. By field experiments Bisen (1969) showed that rice has a

greater power of extrac.ing Fe–P than wheat. When the regression coefficient of Ca–P was taken as one the regression coefficient of Fe–P was about 1·5 times that of Ca–P in wheat soil whereas it was 2·5 times in rice soil. When the extractability of Fe P was taken as one, wheat extracted more Ca-P than rice. The advantage of mobilising effect of rice on soil P was stressed by Takahashi (1965), who showed that the residual effect of P added to a previous crop is much more apparent with rice than with other crops.

The differential effect observed for the two crops on the preference for the P fractions is also reflected in the changes of the available P status as measured by the two soil test methods. After the growth of rice, using superphosphate as the source of P fertilizer there is an increase in Olsen's P and an enrichment of Ca–P. On the other hand, after the growth of wheat there is an increase in Bray's P and decrease in Olsen's P. It is evident that in growing rice after rice continuously there will be a wasteful accumulation of Ca–P while with crops like wheat after wheat there will be a wasteful accumulation of Fe–P whereas the effect of wheat-rice rotation will be complementary leading to a greater efficiency in the utilisation of soil phosphate and reduction in the cost of fertilizer phosphorus needed for crop production.

Interesting distribution pattern of the forms of K also occurs as a result of wheat-rice rotation (Table 3). After the first wheat crop, the fixed K has decreased to a considerable degree along with a slight decrease in exchangeable K and increase in water soluble K. After the third wheat crop also the decrease in fixed K is considerable with a slight increase in exchangeable K only. On the other hand, after the growth of rice there is an increase in fixed K at the expense of depletion in both water soluble and exchangeable K. Thus due to the complementary effect of these two crops, the balance between the different forms of K is restored in a wheat–rice rotation leading to a non accumulation of any form of K. The advantage of changing the crop rotation to offset the high K fixation in soils and utilise the native soil K has been pointed out by Schuffelen and Van Der Marel (1955).

TABLE 3

Effect of crop rotation on forms of soil potassium
(ppm. K. Air dry soil)

Particulars	Water Soluble K	Exchangeable K	Fixed K
(1) Uncropped soil	25	225	1175
	+	–	–
(2) After wheat 1967–68	37	212	1100
	–	–	+
(3) After rice 1968	25	175	1150
	=	+	–
(4) After wheat 1968–69	27	187	1050
	–	–	+
(5) After rice 1969	12	150	1114

TABLE 4

Effect of crop rotation on available trace elements in soil

Particulars	Available content in ppm of Cu	Zn	Mn
(1) Uncropped soil	2·29	1·36	10·78
	=	=	=
(2) After wheat 1967–68	2·55	1·82	12·32
	–	+	+
(3) After rice 1968	1·17	3·55	18·48
	=	=	=
(4) After wheat 1968-69	1·17	2·92	20·02
		+	+
(5) After rice 1969	–	5·00	44·00

The trace elements status of the cropped soil (Table 4) showed that at the doses tried there was a decrease in the status of available Cu caused by the growth of rice. But, there was an over-all increase in the available Zn and Mn status, an effect caused to a greater degree by rice than wheat.

Summary

The relative changes in the distribution of the forms of N, P and K and available nutrients in alluvial soils of Delhi state caused by growing wheat and rice in rotation was studied under pot-culture conditions. There was no change in the status of exchangeable NH^{+}_{4}, NO^{-}_{3} and fixed NH^{+}_{4}. Amino acid N was found to decrease after wheat but increase after rice. Fe–P was found to decrease after wheat but increase after rice. Saloid P was on the other hand found to follow the reverse trend. Similarly Olsen's P was found to decrease after the growth of wheat but Bray's P was found to increase. The reverse trend was found to occur after the growth of rice. There was no change in the levels of occluded forms of phosphorus. Fixed K was found to decrease after wheat but increase after rice. At the doses tried, there was a decrease in available Cu caused by the growth of rice and an over-all increase in the available Zn and Mn status, an effect caused to a greater degree by rice than wheat. It is demonstrated that wheat and rice grown in rotation play a complementary role in making better utilisation of the available forms of major and minor nutrients from the soils, offsetting some of the relative depletions and accumulations caused by growing crops like wheat or rice one after another.

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Kinetics and Mechanism of the Reduction of Ethyl-Methyl Ketone by Titanous Ions

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The view of Burton[1] and Ingold and work done by Muller[2] and Henning and Kimball[3] in connection with heterogeneous reduction of ketone on mercury cathode surface has been elaborated and applied to the present investigation. The reaction is observed to be of the zero order with respect to ethyl-methyl ketone and first order with respect to titanous ion. Keto-enol transformation is not applicable in determining the rate of reaction. It is ketonic variety of the ketone which is involved in the rate determining step.

Materials Employed

Ethyl-methyl ketone (Analar B. D. H. grade), titanous sulphate (Technical B. D. H. grade), ferric chloride (L. R., B. D. H. grade) Ammonium thiocyanate (Analar B. D. H. grade), sulphuric acid (Analar B. D. H. grade) and apparatus for continuous supply of carbon dioxide current.

Ethyl-methyl ketone was redistilled and the fractions distilling between 80-81°C was used. The standard solution of ethyl-methyl ketone was prepared by weighing exact quantity and dissolving in air-free distilled water and stored in dark air-tight bottle. Titanous sulphate solution was prepared and standardised as described by Idem[4] and was stored in air-free carbon dioxide atmosphere. A standard solution of ferric chloride was used in all experiments for quenching the reaction.

Kinetic Measurements

The p esent kinetic study and the results observed are confined to only oxygen free and dark reactions. Reactants free from oxygen were taken in separate specially designed blackend reaction vessels and kept in a thermostat maintained at desired temperature by an electronic relay. Reaction was started by mixing the reactants. A stream of carbon dioxide was continuously passed over the surface of the reaction mixture through out the entire course of the reaction. 5 mls. of the aliquot was taken out at various intervals and poured in a specially designed conical flask containing a known excess of fe ric chloride solution and 25 mls. of 0·5 M sulphuric acid for quenching the reaction and to obviate any possibility of hydrolysis of titanous salt due to dilution. The amount of remaining ferric salt was determined by titrating against a standard solution of titanous sulphate using ammonium thiocyanate as indicator in carbon dioxide atmosphere.

Results

In the present experiment the concentration of titanous ion is small as compared to that of ethyl-methyl ketone. It has been observed that the order of

the reaction with respect to titanous ion is unity. The results obtained show that first order velocity constants remained practically constant in all cases.

The data in Table 1 shows that the value of k_1 the first order velocity constant remains practically constant through out the entire course of the reaction studied.

TABLE 1

$[Ti^{+++}]$ = $4{\cdot}0 \times 10^{-3}$ M. Temperature 40°C.
$[C_2H_5CO.CH_3]$ = $21{\cdot}5 \times 10^{-2}$ M.
$[H_2SO_4]$ = 2·0 M.

Time in minutes	Mls. of 0·0078 M $Ti_2(SO_4)_3$ used	$k_1 \times 10^4$ in minute^{-1}
0	10·30	–
30	10·72	61·10
60	10·82	36·17
90	10·96	34·65
120	11·16	34·13
150	11·36	35·99
180	11·50	35·15
210	11·60	33·75
240	11·72	33·71
270	11·84	34·09
∞	12·80 (Calculated)	–

Average value of k_1 (except first) = $34{\cdot}96 \times 10^{-4}$ minute^{-1}

In Table 2, the data obtained at different initial concentrations of titanous ion, at a given concentration of ethyl–methyl ketone and sulphuric acid has been reported. The data clearly shows that the first order velocity constant is independent of initial concentration of titanous ion.

TABLE 2

$[C_2H_5CO.CH_3]$ = $10{\cdot}75 \times 10^{-2}$M. Temperature 40°C.
$[H_2SO_4]$ = 2·0 M

$[Ti^{+++}] \times 10^3$M	$k_1 \times 10^4$ (min.$^{-1}$)	Half time period $t_{0{\cdot}5}$ (min.)
3·30	35·94	195
4·00	35·44	195
6·60	35·19	195

Average value of k_1 = $35{\cdot}53 \times 10^{-4}$ min^{-1}.

In Table 2, the half time period $t_{0{\cdot}5}$ has also been calculated which is practically constant. The data confirm that the order of reaction with respect to titanous ion is unity in the reaction between ethyl-methyl ketone and titanous sulphate.

The order of reaction with respect to ethyl-methyl ketone.

As the concentration of ethyl-methyl ketone is large as compared to titanous ion, the concentration of ethyl-methyl ketone may be assumed to be constant for any given run. If the initial concentration of the ethyl-methyl ketone is altered, the value of k_1 will change with the change in the initial concentration of ketone. The magnitude of the change in the constant will depend upon the order of the reaction with respect to ethyl-methyl ketone. Table 3, shows that the value of k_1 is practically constant and does not change with the change in the initial concentration of ethyl-methyl ketone. This shows that the order of the reaction with respect to ethyl-methyl ketone is zero. Hence it is concluded that the order of the reaction with respect to ethyl-methyl ketone is zero. It has been shown in Table 1 and 2 that the order of reaction is unity with respect to titanous salt. Therefore, the total order of the reaction is also unity.

TABLE 3

$[Ti^{+++}] = 5{\cdot}0 \times 10^{-3}$M. Temperature 40°C

$[H_2SO_4] = 2{\cdot}0$ M

[Ethyl–methyl ketone] $\times 10^2$M	$k_1 \times 10^4$ (min^{-1}).
5·38	35·65
7·17	35·49
10·75	35·53
21·50	35·25

Average value of $k_1 = 35{\cdot}48 \times 10^{-4}$ min^{-1}.

Table 4, shows the effect of H-ion concentration on the reaction rate. It is observed that the first order velocity constant gradually decreases with the increase in the concentration of sulphuric acid.

TABLE 4

$[Ti^{+++}] = 5{\cdot}00 \times 10^{-3}$ M Temperature 40°C

$[C_2H_5CO.CH_3] = 5{\cdot}38 \times 10^{-2}$ M

$[H_2SO_4] \times$ M	$k_1 \times 10^4$ (Min^{-1})	$[H^+] \times k_1 \times 10^4$
1·00	60·11	60·18
1·50	45·06	67·59
2·00	35·65	71·30
3·00	26·35	79·05
4·00	22·34	89·36

It is assumed that the concentration of H–ion produced will be equal to the molar concentration of sulphuric acid initially taken.

Identification of the Products

A large quantity of reaction mixture containing ethyl-methyl ketone titanous sulphate, sulphuric acid and water was kept in a thermostat for two to three days at 50°C in air-tight vessel keeping all neccssary precautions. When the reaction was complete the reaction mixture was distilled to remove remaining ethyl-methyl ketone. Ketone free reaction mixture was then shaken with ether and etherial layer was seperated and ether was evaporated slowly. Solution thus obtained was distilled in micro-distillation apparatus and fraction distilling at 99°C was collected and put to paper chromatographic test by making xanthozenate. The test confirms the presence of sec-butyl alcohol.

Discussion and Mechanism

In view of the experimental results observed in the present work a plausible mechanism for the reaction between ethyl-methyl ketone and titanous salt has been suggested. As the ketones undergo enolisation in presence of acid or base, it is obvious to enquire whether enolisation of ketone is a rate controlling step or not, in the present series of work. Lapworth[5] is first to point out that the rate controlling process in acetone-bromine reaction involves the slow enolisation of acetone. In their study of enolisation of acetone Dawson and Spirey[6] showed that enolisation is due to general acid base catalysis[7] and in the acetate buffers the rate constant can be given by the expression

$$k_1 = 6\times10^{-9} + 5{\cdot}6\times10^{-4}\ [H_3O^+] + 1{\cdot}3\times10^{-6}\ [HOAC] + 7[OH^-] + 3{\cdot}3\times10^{-6}\ [AOC^-] + 3{\cdot}5\times10^{-6}\ [HOAC]\ AOC^-] \tag{1}$$

In the present case the mixture is highly acidic and does not contain acetic acid or acetate ions. Consequently all the terms except second may be dropped on the right hand side of Eqn. (1). Thus Eqn. (1) can be put in the form :

$$k = 5{\cdot}6 \times 10^{-4}\,[H_3O^+] + k'\,[HSO_4^-] \tag{2}$$

where k' is the catalytic coefficient of HSO_4^- ions (which is included in present case). However, HSO_4^- behaves like weak acid[8] ($K_\alpha = 10^{-2}$ at 25°C). Consequently the catalytic coefficient of 'HSO_4 ion is, nearly equal to that of acetic acid. Thus neglecting second term in Eqn. (2)

$$k = 5{\cdot}6 \times 10^{-4}\,[H_3O^+] \text{ at } 25°C \tag{3}$$

Since each molecule of sulphuric acid gives one H-ion and one HSO_4^- ion on dissociation, the concentration of each ion will be approximately equal to that of sulphuric acid (2M). Hence the rate constant for enolisation of acetone in the presence of 2M sulphuric acid at 25°C will be

$$k = 5{\cdot}6 \times 2 \times 10^{-4} \text{ approximately} \tag{4}$$

As uming the temperature coefficient of enolisation to be 3 for a rise of ten degrees, the rate constant for enolisation at 35°C will be $33{\cdot}6 \times 10^{-4}$ approximately.

It is well known that rate constant of enolisation of ethyl-methyl ketone is very small as compared to acetone. Hence rate constant of enolisation of ethyl-methyl ketone will be very much less than $33{\cdot}6 \times 10^{-4}$ at 33°C.

Present investigation shows that the rate constant of reaction between ethyl-methyl ketone and titanous ion at 40°C is $35{\cdot}48 \times 10^{-4}$ min^{-1}, (see table 3) which will be much higher than the calculated rate constant for enolisation of

ethyl-methyl ketone. Hence enolisation of a ethyl-methyl ketone does not appear to be the rate controlling step in the present series of reactions.

It has been observed that increase in concentration of acid leads to retardation in the reaction velocity. This could not occur if enolisation were one of the rate determining steps, since enolisation is accelerated in presence of acids. It is therefore concluded that the ketonic variety of ketone is the reactive species of ethyl-methyl ketone and not the enolic one.

The metallic ions as such rarely exist in aqueous solution. Thus titanous ion[9] in aqueous solution has the form $Ti(H_2O)_6^{+++}$ like ferric ion which has the form $Fe(H_2O)_6^{+++}$. According to Gorin[10], hydrolysis of metallic ion in aqueous solution involves an attack by hydroxyl ion which replaces a water molecule from the co-ordination sphere of the ion and thus the first and second hydrolytc equilibria involving ferric ion will be represented in the form :

$$\text{A.}\quad [Fe(H_2O)_6^{+++}] + [OH^-] \rightleftharpoons [Fe(OH)\,(H_2O)_5^{++}] + H_2O$$

$$\text{B.}\quad [Fe(OH)\,(H_2O)_5^{++}] + [OH^-] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(OH)\,(H_2O)_4^{+}] + H_2O$$

The first equilibrium is rapid while the second is slow one. In second equilibrium the back reaction constant ($k_2 = 0{\cdot}0783$ at 55°C) is small as compared to the forward reaction constant ($k_1 = 5{\cdot}9 \times 10$ at 55°C) and thus, equilibrium may take finite time before they are fully established and compete with rate determining steps in the reaction between stannous ion and ferric ion. As mentioned, it appears that in the present series of reactions the first step in the reaction mechanism is the slow hydrolysis of titanous ions.

Muller[11], Henning and Kimball[12], have put forward a mechanism for the formation of iso- propyl alcohol at mercury cathode in their study of electrolytic reduction of acetone. Henning and Kimball showed that there is a formation of a surface complex and the uptake of hydrogen in the form of H-ion because even in direct reduction of ketones by dissolving metals a direct addition of hydrogen does not take place. Burton and Ingold[13] developed the theory that the "Nascent" hydrogen of dissolving metals consists of the electrons and protons supplied from different sources but not of preformed H-atoms. The reduction of ketone by metals capable of forming bivalent ion occurs when two electrons have been captured by organic system, when octets have been completed and a negative charge has been acquired by the organic system.

On the basis of what has been described earlier the following mechanism is suggested :

$$\text{C.}\quad [Ti(H_2O)_6^{+++}] + [OH^-] \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} [Ti(OH)\,(H_2O)_5^{++}] + H_2O$$

$$\text{D.}\quad [Ti(OH)\,(H_2O)_5^{++}] + \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\!C=O \xrightarrow{k_2} [Ti(OH)\,(H_2O)_5^{++}] + \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\!\dot{C}\text{-}O^{\cdot}$$

$$\text{E.}\quad \begin{matrix} H_5C \\ H_3C \end{matrix}\!\!>\!\dot{C}\text{-}O^{\cdot} + H_2O \xrightarrow{\text{fast}} \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\!\dot{C}\text{-}OH + [OH^-]$$

$$\text{F.}\quad \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\dot{C}\text{-}OH + [Ti(OH)(H_2O)_5^{++}] \xrightarrow{\text{fast}} \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\ddot{C}\text{-}OH + [Ti(OH)(H_2O)_5^{+++}]$$

$$\text{G.}\quad \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\ddot{C}\text{-}OH + H_2O \xrightarrow{\text{fast}} \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>CHOH + [OH^-]$$

In the mechanism mentioned above the first two steps are rate determining steps. The last three steps are fast and need not be taken into consideration for calculating the rate reaction.

The rate, at which the concentration of titanous ion changes will be given by the expression :

$$-\frac{d[Ti(H_2O)_6^{+++}]}{dt} = k_2[Ti(OH)(H_2O)_5^{++}] \times [H_5C_2\text{-}CO\text{-}CH_3] \qquad (5)$$

where $[Ti(OH)(H_2O)_5^{++}]$ represents the stationary state concentration of hydrolysed titanous ion at the stationary point, and therefore

$$-\frac{d[Ti(OH)(H_2O)_5^{++}]}{dt} = k_1'[Ti(H_2O)_6^{+++}] \times [OH^-] - k_{-1}'[Ti(OH)(H_2O)_5^{++}]$$

$$- k_2[Ti(OH)(H_2O)_5^{++}] \times [H_5C_2\text{-}CO\text{-}CH_3] = \qquad (6)$$

$$\text{Or } k_1'[Ti(H_2O)_6^{+++}] \times [OH^-] = k_{-1}'[Ti(OH)(H_2O)_5^{++}] + k_2[Ti(OH)(H_2O)_5^{++}] \times [H_5C.CO.CH_3]$$

$$\text{Or } [Ti(OH)(H_2O)_5^{++}]\{k_{-1}' + k_2[H_5C_2\text{-}CO\text{-}CH_3]\} = k_1'[Ti(H_2O)_6^{+++}] \times [OH^-]$$

$$\text{Or } [Ti(OH)(H_2O)_5^{++}] = \frac{k_1'[Ti(H_2O)_6^{++}] \times [OH^-]}{k_{-1}' + k_2[H_5C_2.CO.CH_3]} \qquad (7)$$

Substituting for $[Ti(OH)(H_2O)_5^{++}]$ in Eqn. (5) the expression becomes :

$$-\frac{d[Ti(H_2O)_6^{+++}]}{dt} = \frac{k_1' k_2 Ti(H_2O)_6^{+++}] \times [H_5C_2.CO.CH_3] \times [OH^-]}{k_{-1}' + k_2[H_5C_2\text{-}CO\text{-}CH]} \qquad (8)$$

$$\text{Now} \qquad [OH^-] = K_w/[H^+] \qquad (9)$$

where K_w is the dissociation constant for water.

Substituting for $[OH^-]$ in Eqn. (8) it becomes

$$-\frac{d[Ti(H_2O)_6^{+++}]}{dt} = \frac{k_1 k_2 K_w[Ti(H_2O)_6^{+++}][H_5C_2.CO.CH_3]}{[H^+]\{k_{-1}' + [H_5C_2.CO.CH_3]k_2\}} \qquad (10)$$

where $[Ti(H_2O)_6^{+++}]$ represent the instantaneous concentration of titanous ions and $[H_5C_2.CO.CH_3]$ represents the concentration of ethyl-methyl ketone. Eqn. (10) clearly shows that the velocity of the reaction will decrease with an increase in H-ion concentration and this has been found to be experimentally correct (*see* Table 4). The experimental results confirm that the value of k_1 decreases with increase in the H-ion concentration although exact inverse proportionality has not been observed. This discrepancy is most probably due to the fact that in calculating the concentration of H-ions, the dissociation of HSO_4^- ion could not be taken into consideration.

Since titanous salts are much more easily hydrolysed than ferric salts, ($k_{-1}' = 0{\cdot}0783$) it is reasonable to assume that the value of k_1' in the case of hydrolysis of titanous ion will be very small. In view of the above arguments, one may assume that the value of k_{-1}' is very small as compared to that of $k_2[H_5C_2.CO.CH_3]$ in Eqn. (10).

Thus Eqn. (10) can be written as :

$$-\frac{d[Ti(H_2O)_6^{+++}]}{dt} = \frac{k_1' K_w[Ti(H_2O)_6^{+++}]}{[H^+]} \qquad (11)$$

For any given hydrogen ion concentration the Eqn. (11) can be put in the form :

$$-\frac{d[Ti(H_2O)_6^{+++}]}{dt} = k_1[Ti(H_2O)_6^{+++}] \qquad (12)$$

where k_1 is experimentally observed first order velocity constant and is expressed by :

$$k_1 = \frac{k_1' K_w}{[H^+]}. \qquad (13)$$

Eqn. (11) clearly shows that the reaction is independent of the concentration of ethyl methyl ketone and the reaction is inversely proportional to the concentration of H-ions. Eqn. (12) also shows that the order of the reaction with respect to titanous ion is unity and with respect to ethyl-methyl ketone is zero. Hence the mechanism put forward seems to be quite reasonably correct and explains the observed data.

Acknowledgement

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Kinetics of Hydrolysis of Dibromo-acetate Ion in Alkaline Aqueous medium

By

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[Received on 8th November, 1968]

Abstract

Hydrolysis of dibromo-acetate ion in alkaline aqueous medium has been studied. The order of the reaction is two, unity with respect to each reactant while in neutral medium kinetic course of the reaction shows the first order. The reaction has been studied at four different temperatures. A plausible mechanism of hydrolysis in alkaline medium has been put forward.

Introduction

Larson[1] has studied the hydrolysis of dichloroacetate ion in aqueous alkaline medium at 75°. According to F. Kunze[2] the dichloro-acetate ions, not dichloro-acetic acid molecules, are hydrolysed in acidic or faintly alkaline aqueous medium. He showed the order of the reaction is unity and is not catalysed by hydrogen ions. It has also been shown by Larson that first order process does not show phosphate ion catalysis. Here the hydrolysis of dibromo-acetate ion has been studied and it has been found that it hydrolyses more rapidly than dichloro-acetate ion. It has been found that order of the reaction is two, unity with respect to each reactant and in neutral medium or in faintly alkaline medium the order is unity.

Material employed: Sodium dibromo-acetate (Fluka) was used as such, sodium hydroxide, potassium nitrate, silver nitrate, ammonium thiocyanate and feric alum were all either (A. R. B. D. H.) or (G. R. E. Merck) grade.

Progress of the reaction: The reaction was studied at the requisite temperature by keeping it in a thermostat. The progress of the reaction was quenched by pouring an aliquot part (5 ml.) to a beaker containing 10 ml. of 3N nitric acid. A known amount of $AgNO_3$ was added and the excess was estimated by standard solution of ammonium thio-cyanate using ferric alum as an indicator.

Study of hydrolysis in neutral solution:

The reaction was also studied in faintely alkaline solution, under these conditions the reaction velocity is slow. Here also the progress of the reaction was followed by estimating the bromide ion formed.

The overall reaction between dibromo-acetate ion and hydroxyl ion may be written as follows :

$$CHBr_2COO^- + 2OH^- \rightarrow CHOCOO^- + H_2O + 2Br^- \qquad (1)$$

according to above equation the order of the reaction must be three but in practice it has been found that order is unity with respect to dibromo-acetate ion and is

unity with respect to hydroxyl ion at constant ionic strength. It seems that this reaction is not one step process but two steps reaction, they may be—

$$CHBr_2COO^- + OH^- \rightarrow CH(OH)Br\ COO^- + Br^- \tag{2}$$

$$CH(OH)BrCOO^- + OH^- \rightarrow CHOCOO^- + Br^- + H_2O \tag{3}$$

of which (3) in comparision to (2) proceeds so rapidly that (2) determines the rate of hydrolysis. Here the hydrolysis is a reaction of the second order. The kinetical experiments show that the rate is according to (2) proportional to the concentration of dibrom-acetate ion and hydroxyl ions at constant ionic strength when the solutions are so alkaline that the hydrolysis in neutral medium can be ignored. The rate of the reaction can be expressed by following expression :

$$-\frac{dc}{dt} = k_2\,[OH^-]\,[CHBr_2\ COO^-] \tag{4}$$

This equation only holds good initial region of the reaction. We have confined·ourself only in initial of the reaction due to the fact that in finite quantity of hydroxyl ions secondary reaction between glyoxate ion and hydroxyl ions takes place according to the following equation :

$$2CHOCOO^- + OH^- \rightarrow \begin{array}{c} CH_2OH \\ | \\ COO^- \end{array} + \begin{array}{c} COO^- \\ | \\ COO^- \end{array}$$

The velocity constant can be calculated by dividing the value of initial velocity $(-\frac{dc}{dt})$ with the concentration of dibromo-acetate ion and hydroxyl ion.

In following tables the column 1 shows the initial concentration of dibromoacetate ion ; column 2 shows the concentration of dibromo-acetate at which the velocity is measured ; column 3 shows the value of $(-\frac{dc}{dt})/C = k_1$ which is practically constant proves that the order of the reaction with respect to dibromo-acetate ion is unity.

TABLE 1

(A)

Temperature 55°C

[Sodium Hydroxide] = 4M

$[CHBr_2COO^-] \times 10^2$M	$C \times 10^2$M	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ litres mol^{-1} min^{-1}
5·06	4·63	8·01	2·00
3·54	3·21	8·12	2·03
2·56	2·34	8·10	2·02
1·60	1·48	8·10	2·02
0·70	0·64	8·09	2·02

(B)

Temperature 50°

[Sodium hydroxide] = 4M

$[CHBr_2COO^-] \times 10^2M$	$C \times 10^2M$	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ litres mol^{-1} min^{-1}
5·06	4·77	5·87	1·47
3·54	3·33	5·85	1·46
2·56	2·39	5·94	1·48
1·60	1·19	5·86	1·46
0·70	0·71	5·89	1·47

According to assumed steps of the reaction the velocity of the reaction should also proportional to the hydroxyl concentration to test this the series of the experiments have been performed with the different concentration of hydroxyl ion.

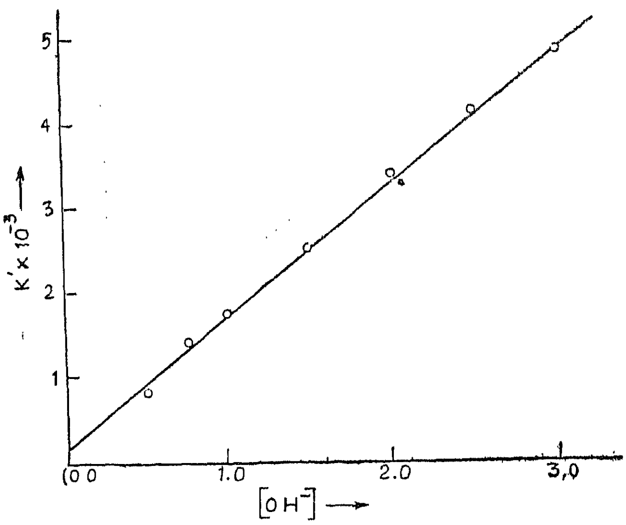

TABLE 2

Temperature 55°

$[CHBr_2COO^-] = 5{\cdot}06 \times 10^{-2}M$

$[OH^-] \times M$	$k_2 \times 10^4$ litres mol^{-1} min^{-1}
5·00	27·70
4·00	20·40
3·00	16·20
2·00	13·80
1·50	11·70
1·00	8·80

It is evident from above table that as the concentration of hydroxyl ions is decreased the value of k_2 also decreases. This shows that the ionic strength of the reaction mixture is so high that the rate equation (4) can not be more strictly fulfilled. In following table the concentration of hydroxyl ion is varied by keeping the ionic strength of the medium constant by addition of potassium nitrate. Now the value of k_2 is quite constant which shows that the velocity is also directly proportional to hydroxyl ion.

TABLE 3

Temperature 55°

$[CHBr_2\,COO^-] = 5{\cdot}06 \times 10^{-2}M$

$\mu = 3\,M$

$[OH^-] \times M$	$k_2 \times 10^3$ litres mol^{-1} min^{-1}
3·00	1·62
2·50	1·64
2·00	1·68
1·50	1·65
1·00	1·60
0·75	1·62
0·50	1·65

This k_2 is not true second order rate constant. The value of true second order rate constant ($\bar{k}_2$) can be calculated with the help of following equation[3].

$$\bar{k}_2 = \bar{k}_2 \quad \frac{k_1}{(b-x)} \tag{6}$$

where k_1 is first order rate constant and $(b-x)$ decrease in the concentration of hydroxyl ions. In order to find the value of k_1 the experiments were carried out in buffer solution of disodium hydrogen phosphate and potassium dihydrogen phosphate at ionic strength equal to 3 having composition

$$[CHBr_2COO^-] = 5{\cdot}06 \times 10^{-2}M \; ; \; [Na_2HPO_4] = 0{\cdot}02\ M \; ;$$

$[KH_2PO_4] = 0{\cdot}007$ M ; $[NaNO_3] = 2{\cdot}23$ M. The value of first order rate constant comes out to be $1{\cdot}20 \times 10^{-4}\ min^{-1}$. In presence of finite concentration of the hydroxyl ion the contribution overall velocity due to first order process is negligible but still has some contribution. So the total rate of the reaction can be expressed by following expression :

$$-\frac{dc}{dt} = \bar{k}_2\,[CHBr_2COO^-]\,[OH^-] + k_1\,[CHBr_2COO^-] \tag{7}$$

$$\frac{-\dfrac{dc}{dt}}{[CHBr_2\ COO^-]} = \bar{k}_2\,[OH^-] + k_1$$

$$k' = \bar{k}_2[\,OH^-] + k_1 \tag{8}$$

In order to find the value of $\overline{k}_2$ and k_1 a graph is plotted (see Fig. 1) between k' and OH^- at constant ionic straight. The strengt line is obtained from which the slope gives the value of $\overline{k}_2$ as $1{\cdot}58 \times 10^{-3}$ litres mole^{-1}min^{-1} and the intercept gives value of k_1 as $1{\cdot}25 \times 10^{-4}$ min^{-1} which is not much different from the value obtained by integral method. Once the value of k_2 and k_1 is known, the value of $\overline{k}_2$ can be calculated with the help of equ. (6), $\overline{k}_2$ comes out to be $1{\cdot}58 \times 10^{-3}$ litre mol^{-1} min^{-1}.

The temperature coefficient of the reaction is nearly 2·63 (See Table IV) so it is easy to calculate the value of $\overline{k}_2$ at 75°. It comes out to be $60{\cdot}84 \times 10^{-4}$ litres mol^{-1} min^{-1} where as the value of k_2 for dichloro-acetate ion is $8{\cdot}0 \times 10^{-4}$ litre mol^{-1} min^{-1}. On comparing these values for chloro and bromo is higher than that of Chloro which is due to the fact that bond energy vary in order C–Cl > C–Br. The value of energy of activation comes out to be 19,490 calories.

TABLE 4

Temperature	$\overline{k}_2 \times 10^{-4}$ litres mol^{1-} min^{1-}
60°	23·80
55°	15·80
50°	8·98
45°	6·10

Isolation of products :

After the completion of the reaction the products were separated with the help of paper chromatography. The method of Stark and Co-workers[4] was employed. The products were glycollic acid and oxalic acid. The intermediate product namely sodium glyoxalate is separated as sodium diphenacyl acetate by addition of acetophenone to the reaction mixture. Reaction takes place according to following equation[5]

$$2C_6H_5COCH_3 + CHO\,COO^-Na^+ \rightarrow (C_6H_5COCH_2)_2\,CHCOO^-Na^+$$

This product is soluble in alcohol. Now this solution is mixed with hydrochloric acid. The diphenacyl acetic acid thus precipitated was dissolved in alkaline solution and again precipitated with hydrochloric acid. The melting point of diphenacyl acetic acid comes out to be 130–132° and the equivalent weight as 296·0 to 296·5 (found), 296·2 (calculated).

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Kinetics of Bromination of some π-Deficient N-Hetero-Aromatics in Carbontetra Chloride Solution

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Abstract

The data obtained in the kinetic study of bromination of 2 : 3 benzoquinoline (acridine) and 5 : 6 benzoquinoline with bromine in non-polar solvent *viz.* carbon tetrachloride have been reported here. In each case the total order of the reaction is two, unity with respect to each reactant. A plausible mechanism of bromination has been put forward.

Introduction

The kinetics of bromination of the π-deficient N-heteroarometics (acridine and 5 : 6 bonzoquinoline) in non-polar solvent *viz.* carbontetrachloride has been studied for the first time. The exact nature of the reaction products when bromine reacts with these aza-aromatics in carbontetrachloride solution at ordinary temperature have been discussed in detail by Acheson, Hoult and Barnard[1], Slough and Ubbelohde[2] and more recently by Eisch[3,4] (in case of quinoline).

In the case of acridine or 5 : 6 benzoquinoline one mole of each requires one mole of bromine. These compounds are stable in non-polar solvent *viz.* carbontetrachloride but gradually decompose in ionizing solvent like water and alcohol. Here the reaction has been studied in carbontetrachloride as solvent the compounds which are formed remain stable throughout entire course of the reaction.

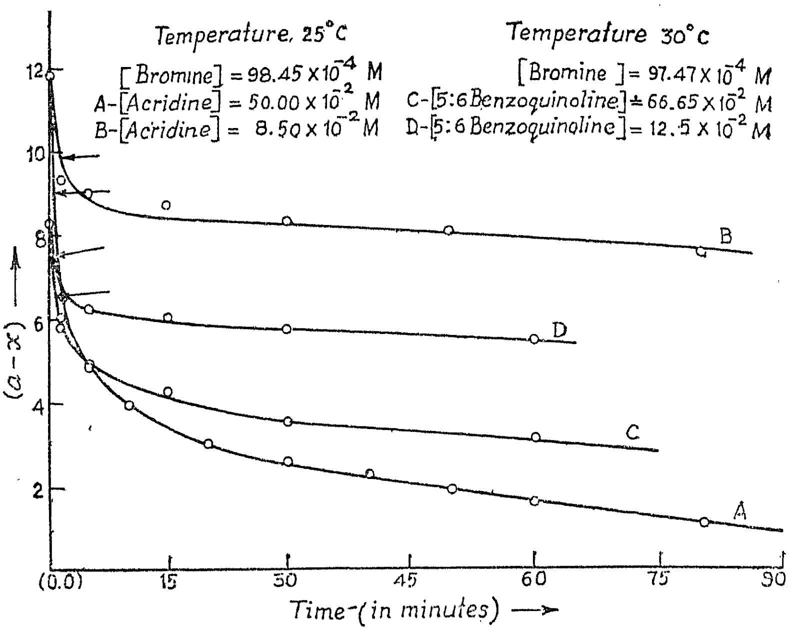
Experimental

L. R. (B. D. H.) garde acridine, G. R. (E. Merk) grade 5 : 6 benzoquinoline and G. R. (E. Merck) grade bromine were employed.

AnalaR (B. D. H.) grade carbontetrachloride after distillation in quick-fit apparatus was employed as solvent potassium iodide and sodium thiosulphate required for titrating were all A. R. (B. D. H.) grade samples.

Kinetic Measurement : The progress of the reaction has been followed exactly in the same way as in the case of isoquinoline and bromine reaction[5].

Results and Discussion : The reaction between bromine and acridine or 5 : 6 benzoqulnoline is very fast and corresponding measurements of the progress of the reaction becomes difficult. An additional difficulty arises owing to the precipitation of the reaction product right from beginning of the reaction. Consequently the rate constant for the initial parts of the reaction alone have been calculated although the progress of the reaction has been followed till about fifty to ninety percent of bromine has been used up.



The total order of the reaction is two, unity with respect to each of the reactants. As the reaction proceeds the reaction mixture becomes more and more heterogeneous due to the precipitation of the product so it is quite possible that some of the bromine may be absorbed on the surface of the reaction product and hence, only initial slopes (*viz.* up to the point where 30% or 50% of the reaction is over) have been found out by drawing graphs between concentration against time and used for calculating the second order constants. The initial rate of disappearance of bromine can be given as

$$-\frac{d[Br_2]}{dt} = k[\text{Bromine}]\ [C] \tag{1}$$

where C stands for acridine or 5 : 6 benzoquinoline and k is second order rate constant. The value of k is determined by dividing the value of $-\frac{d[Br_2]}{dt}$ with the concentration of compound and with concentration of bromine at which the slope is found out. Hence, the equation (1) can be expressed as

$$k = \frac{-\left(\frac{dc}{dt}\right)/2 \times (S/V)}{[\text{Bromine}]^{*}[C]_0}$$

where [Bromine]* represents the concentration of bromine at which the actual slope is measured and $[C]_0$ represents the initial concentration of acridine or 5 : 6 benzoquinoline.

Now the value of $-\frac{dc}{dt}$ is found out by measuring the slope of the curve in initial part of reaction (*See* Fig. 1) and $-\frac{dc}{dt}/2$ represents the slope in terms of molar concentration of bromine. Now $-\frac{dc}{dt}/2 \times S/V$ represents the change

in gram molar concentration of bromine per litre of the solution, here S represents the strength of Hypo (sodium thiosulphate) required for titration and V volume of the reaction mixture withdrawn.

The following table record the data obtained in study of the reaction between acridine and bromine.

TABLE I

Effect of variation of acridine concentration
$[Bromine]_0 = 99{\cdot}70 \times 10^{-4}M$

Temperature	$[acridine]_0$ $\times 10^2M$	[Bromine]* $\times 10^4M$	$\left(\frac{dc}{dt}\right) \times 10$ ml. min^{-1}	$k \times 10$ litres mol^{-1} min^{-1}
40°	50·00	56·35	98·00	30·15
	25·00	60·69	53·40	30·52
	16·50	52·02	32·00	32·31
	10·14	65·02	24·00	31·56
35°	50·00	62·58	90·00	25·71
	25·00	53·68	40·00	26·67
	10·14	71·52	22·00	27·12
	8·50	71·52	17·00	25·00
30°	50·00	60·00	90·00	21·17
	16·50	72·09	32·00	21·55
	10·14	76·09	22·00	22·84
	8·50	72·09	16·60	21·70
25°	50·00	75·06	82·00	18·66
	25·00	75·06	42·00	17·91
	16·50	73·39	26·00	18·23
	8·50	80·06	14·00	17·16

TABLE II

Effect of variation of bromine concentration
$[Acridine]_0 = 12{\cdot}50 \times 10^{-2}M$

Temperature	$[Bromine]_0$ $\times 10^4M$	[Bromine]* $\times 10^4M$	$\left(\frac{dc}{dt}\right) \times 10$ ml. min^{-1}	$k \times$ litres mole^{-1} min^{-1}
40°	130·80	81·18	36·00	32·00
	99·70	60·18	29·00	33·14
	69·60	43·36	36·00	35·99
	49·12	32·12	20·00	34·07
35°	96·56	59·00	22·00	26·67
	68·69	49·60	14·00	28·00
	49·12	34·20	17·00	27·20
30°	98·05	64·08	22·00	22·02
	68·64	49·92	17·00	20·61
	50·17	34·20	20·00	21·59
25°	134·50	111·00	28·00	18·66
	98·45	79·23	22·00	18·61
	66·52	52·25	26·00	18·16

TABLE III

Effect of variation of 5 : 6 Benzoquinoline concentration

[Bromine]$_0$ = 99·50 × $10^{-4}M$

Temperature	[5 : 6 Benzo-quinoline] × 10^2M	[Bromine]* × $10^{-4}M$	$\left(\frac{dc}{dt}\right)$ × 10 ml. min^{-1}	k × 10 litres mol^{-1} min^{-1}
40°	66·65	67·97	64·00	13·71
	40·00	82·53	48·00	14·11
	20·00	87 38	28·00	15·52
	12·50	82·53	16·00	15·05
35°	66·65	74·88	30·00	5·30
	20·00	79·26	10·60	7·41
	12·50	81·05	8·00	6·99
	[Bromine]$_0$ = 97·47 × $10^{-4}M$			
30°	66·65	76·70	34·00	7·85
	20·00	88·50	14·20	9·47
	12·50	88·50	8·50	9 07
	[Bromine]$_0$ = 96·78 × $10^{-4}M$			
25°	66·65	74·16	90·00	16·88
	40·00	75·08	52·00	16·04
	20·00	74·16	28·00	17·50
	12·50	84·43	17·00	15·11

TABLE IV

Effect of variation of Bromine concentration

[5 : 6 Benzoquinoline]$_0$ = 10·00 × $10^{-2}M$

Temperature	[Bromine]$_0$ × 10^4M	[Bromine]* × 10^4M	$\left(\frac{dc}{dt}\right)$ × 10 ml. min^{-1}	k × 10 litres mol^{-1} min^{-1}
40°	51·48	37·50	8·56	14·27
	66·75	55·12	13·00	14·73
	99·50	82·53	11·00	12·94
	125·6	108·80	16 60	12·57
35°	51·39	40·26	3·74	6·80
	65·12	55·08	3·33	7·37
	98·85	76·95	5·40	6·09
	126·20	104·70	7·00	5·30
30°	68·77	56·16	9·00	9·99
	97·47	84·96	6·40	8·89
	133·4	106·60	7·60	8·94
25°	125·60	112·10	16·20	18·23
	96·78	78·80	15·00	17·65
	66·30	55·08	9 00	16 65
	50·05	40·50	13·00	17·33

A perusal of above tables shows that the value of second order rate constant (k) remains practically constant from one reaction to the other at constant temperature, showing thereby the validity of the equation (1). It is evident from the tables I and II in the case of acridine that as the temperature is increased the velocity of the reaction also increases and energy of activation comes out to be 8·55 K, cals. On the other hand from tables III and IV in case of 5 : 6 benzoquinoline it is quite clear that as the temperature is increased velocity of the reaction decreases due to the fact that the product may namely 5 : 6 benzoquinoline dibromide decompose at these temperatures but as temperature is still higher the velocity increases. This may be due to the substitution of bromine in the ring of the compound, although this has not been investigated.

The reaction between bromine and acridine or 5 : 6 benzoquinoline may be represented by following steps :

$$C + Br_2 \overset{K}{\rightleftharpoons} C\,Br_2^*$$

$$C\,Br_2^* \xrightarrow{k_1} C.\,Br_2$$

where C stands for acridine or 5 : 6 benzoquinoline and $C\,Br_2^*$ may be regarded as an intermediate. Hence the rate of the reaction will be given by

$$-\frac{d[Br_2]}{dt} = k_1\,[C\,.\,Br_2^*] \qquad (2)$$

Now the equilibrium concentration of $[C.\,Br_2^*]$ will be given by

$$[C.\,Br_2^*] = K\,[C]\,[Br_2]$$

by substituting the value of $[C.\,Br_2^*]$ in equn (2)

$$\frac{-d[Br_2]}{dt} = k_1\,K\,[C]\,[Br_2]$$

$$= k\,[C]\,[Br_2] \qquad (3)$$

which is a simple second order expression as has been confirmed by the measurements of the constents in the initial part of the reaction. This mechanism, therefrom adequately explain the present kinetic data.

Acknowledgements

Y. P. S. Tomar and K. Behari wish to thank the U. P. C. S. I. R. and University Grants Commission India for providing financial assistance.

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Chemical Examination of the Pods of *Cassia fistula* Linn.

By

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Abstract

During the chemical investigation of the pods of *Cassia fistula* a wax and a disaccharide have been isolated and studied. The petroleum ether extract deposited a waxy residue which was separated by filtration and purified. Saponification of the purified wax, m.p. 84-85°, yielded lignoceric acid, *n*-triacontanol and *n*-triacontane-1, 30-diol. From the analytical data, the wax was found to consist of 57·2% of *n*-triacontyl lignocerate and 42·8% of delignocerate of *n*-triacontane-1, 30-diol. The alcoholic extract of the defatted pods gave a crystalline disaccharide which was identified to be sucrose.

Introduction

Cassia fistula (N. O. Caesalpiniaceae), commonly known as Amaltas in Hindi, is highly reputed for the medicinal uses of its different parts.[1] In the fruit pulp, Pal Lipták and Iren Széntgáli[2] have reported the presence of a yellow substance that became red on the addition of alkali but according to them micro-sublimation could not prove the presence of hydroxymethylanthraquinone. It also contains 1, 8-dihydroxyanthraquinone, rhein, sennosides *A* and *B*.[3,4] Karim[5] and Sacco[6] have found the presence of an unsaturated hydrocarbon wax, aloin, barbaloin, a glucoside of hydroxymethoxyanthraquinone (unidentified) and a free or combined hydroxymethylanthraquinone. The present work was taken up to reinvestigate the chemical constituents of the pods of *Cassia fistula.*

Experimental and Results

Extraction with Petroleum-ether and separation of the Waxy Matter :

The dried and powdered pods (5 kg) of *C. fistula* were exhaustively extracted with petroleum ether (40-60°). Concentration of the extracts deposited a waxy substance (20 g, m.p. 78-80°) which was filtered, washed repeatedly with ether and purified through repeated crystallisations giving a waxy solid (10 g), m.p. 84–85°.

Study of the Wax :

The white wax gave a single spot (Rf 0·89 and 0·93) on thin-layers of silica gel *G* in chloroform and chloroform-methanol (8 : 2). Infra-red spectra of the compound indicated the presence of carbonyl function (5·75 μ ; 1730 cm^{-1}) proved to be an ester as the hydrolysis of wax (5 g) with 10% alcoholic KOH gave an acid and a mixture of alcohols.

(A) Characterisation of the Acid :

The acid (1·2 g ; S. E., 376), $C_{24}H_{48}O_2$, m.p. 85-86°, should ν_{max}^{KBr} 1695 cm^{-1} (COOH) and gave single spot on TLC in ethanol-water (75 : 25), acetone and acetone-chloroform (9 : 1). It was found to be saturated and formed a methyl ester*, $C_{25}H_{50}O_2$, m.p. 58–59°. These chemical and physical evidences together with paper partition chromatograpy[7,8] established the identity of the acid as lignoceric acid which was further substantiated by m.m.p. determination and co-chromatography with an authentic specimen.

(B) Separation of the Alcohols :

TLC of the neutral portion from the saponification of the wax on silica gel *G* in chloroform-methanol (7 : 3) gave two spots. Column chromatography over activated alumina gave alcohols *A* and *B* by elution with pet.–ether (40-60°)-benzene mixture and chloroform respectively.

(a) Examination of the Alcohol A :

The alcohol *A** (900 mg), $C_{30}H_{62}O$, m.p. 85° after recrystallisation from benzene, was found to be pure by TLC in benzene–methanol (99 : 1) mixture and showed ν_{max}^{KBr} 3450 cm^{-1} (OH). It did not give Liebermann-Burchardt test for sterol or triterpene and also bromine test for unsaturation but formed an acetate*, $C_{32}H_{64}O_2$, m.p. 69–70°. Oxidation of the alcohol (300 mg) with conc. nitric acid over a water-bath for about 3 hours gave an acid*, $C_{30}H_{60}O_2$; m.p. 92–93° after crystallisation from hot methanol. The mol. wt. (448) of the acid was determined by titration method.[9] Thus, it is evident that the alcohol *A* contains a primary hydroxyl group. From these studies alcohol *A* was identified as *n*–triacontanol.[10]

(b) Examinotion of the Alcohol B :

The alcohol *B** (600 mg), $C_{30}H_{62}O_2$, m.p. 112–113° after repeated crystallisations from cloroform-methanol, was found to be single entity by TLC in solvents consisting of chloroform and methanol. It gave negative tests for unsaturation but formed a diacetate*, $C_{34}H_{66}O_4$, m.p. 79-80° and showed ν_{max}^{KBr} 3450 cm^{-1} (OH). Nitric acid oxidation of the alcohol (300 mg) gave a dibasic acid, $C_{30}H_{58}O_4$, which was worked up as usual and crystallised from petroleum ether to yield white crystals (150 mg), m.p. 121–122° and S. E.[9], 233·6. The acid (90 mg) formed an ethyl ester*, $C_{34}H_{66}O_4$, m.p. 73-74° and S. E.[11], 264. Thus the acid was identified as octacosane–1, 28–dicarboxylic acid[12,13] and the alcohol *B* as *n*–triacontane-1, 30-diol.

Isolation and the study of the Disaccharide :

Alcoholic extract of the defatted pods of *C. fistula* deposited a crystalline solid which on purification and crystallisation from aqueous alcohol gave cubical crystals* (200 g), $C_{12}H_{22}O_{11}$, m.p. 185–186°, $[\alpha]_D^{25}$ + 65·13° (water), ν_{max}^{KBr} 3550, 1460 and 1020 cm^{-1} (OH). Hydrolysis with acid followed by qualitative examination of the hydrolysate on paper[14,15] and thin-layers[16] and quantitative estimation by the periodate method[17] showed the presence of D-glucose and D-fructose in the molecular ratio of 1 : 1. The disaccharide formed an Octaacetate, m.p. 71–72°, $[\alpha]_D^{25}$ + 58·4° ($CHCl_3$) and an octamethyl ether, $[\alpha]_D^{25}$ + 66·8° (methanol). Thus the disaccharide (a non-reducing sugar) was inferred to be sucrose which was finally identified by Co-chromatography and m.m.p. determination with an authentic sample.

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* Elemental analysis and analytical data agreed well with the theoretical values.

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Hydromagnetic free convection from a suddenly heated horizontal flat plate

By

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Abstract

Free convection flow following a sudden rise in the temperature of a horizontal semi-infinite flat plate, immersed in an electrically conducting fluid otherwise at rest, and with a magnetic field perpendicular to the plane of the plate, is studied. Simple velocity and temperature profiles are assumed and the time dependent components of the velocity and temperature are separated. It is found that the magnetic field reduces the free convection flow, whereas the heat transfer is not appreciably affected.

Nomenclature

A, Factor defined by the equation (6)
a, Power index defined by the equation (6)
B Magnetic Induction
F Time dependent velocity function
G Time dependent temperature function
Gr, Grashof number
g, Acceleration due to gravity
L, Characteristic length
m, Power index defined by the equation (14)
N, Interaction parameter
p Dynamic pressure
P_r Prandtl number
q, Power index defined in the transformation (14)
r, Power index defined in the transformation (14)
s, Power index defined in the transformation (14)
T, Temperature inside the boundary layer
T_∞, Temperature of the ambient fluid
T_w, Wall temperature
t, Time
U, Characteristic velocity
u, Component of the velocity along the x axis
u_1, Time dependent component of the velocity defined by equ. (9)
v, Component of the velocity along the y-axis
x, Coordinate along the x-axis
y, Coordinate along the y axis

Greek symbols

α, Thermal diffusivity

β, Expansion coefficient

δ, Boundary layer thickness

θ, Dimension less temperature $\left(= \frac{T-T_\infty}{T_w-T_\infty}\right)$

θ_1, Time dependent component of the temperature

ν, Kinematic viscosity

τ, Similarity variable defined in the equation (14)

ρ, Ambient fluid density

σ, Electrical conductivity

Subscript

$'$, First differentiation with respect to τ

1. Introduction : In practice cases where there is an uncontrolled transient rise in the temperature of the fluid carrying devices are of importances. The effect of such temperature rise on an electrically conducting, incompressible fluid is studied in this paper, taking a simple case of a semi-infinite horizontal flate plate with a transverse magnetic field imposed upon it.

A horizontal semi-infinite flat plate has a stationary electrically conducting fluid over it and a magnetic field is applied transverse to the plane of the plate. Initially, the plate and the fluid are at the same temperature. Suddenly the plate-temperature rises to the value T_w ($> T_\infty$). The temperature of the plate drops to the orginal value immediately afterwards. Free convection ensues using Boussinesq approximation, the change in the density of the fluid due to the rise in temperature is taken into account in the buoyancy term only, which puts a limit on the value of $T_w - T_\infty$.

The magnetic field and the temperature vary along the plate in a fashion imposed by the requirements of the similarity solution of the equations for the time dependent components of the velocity and temperature. Such a magnetic field can be realized in practice by suitably arranging the current carrying loops.

Magnetic Reynolds number is assumed to be small and therefore the induced magnetic field has been neglected. This assumption is valid for most of the liquids of practical importance.

Approximate velocity and temperature profiles used by Gupta (1) in the similar steady flow problem have been assumed and by similarity transformation, the partial differential equations for the time dependent components of velocity and temperature have been transformed into ordinary differential equations. These equations have been solved on IBM 7044 digital computor at I.I.T. Kanpur.

Gupta (1) has analysed the steady magnetohydrodynamic free convection with transverse magnetic field on a horizontal flat plate. Transient flow problems in the hydrodynamic case for compressible and incompressible fluids have been studied by Riley (2,3)

2. Basic equations : The plate immersed horizontally in an electrically conducting fluid at the temperature T_∞, with a transverse magnetic field impressed upon it, gets suddenly heated to a temperature T_w ($> T_\infty$) at the time $t = 0+$. The plate drops to the temperature T_∞ immediately afterwards. Let the x-axis be along the plate and the y-axis perpendicular to it with the origin at the leading edge. The boundary layer equations of continuity, momentum and energy are

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}$$

$$\frac{\partial u}{\partial t} + u.\frac{\partial u}{\partial x} + v.\frac{\partial u}{\partial y} = g\ \beta\ \frac{\partial}{\partial x}\int_y^{\delta} (T - T_{\infty})\ dy + \nu\ \frac{\partial^2 u}{\partial y^2} - \frac{\sigma B^2 u}{\rho_{\infty}} \tag{2}$$

and

$$\frac{\partial T}{\partial t} + u.\frac{\partial T}{\partial x} + v.\frac{\partial T}{\partial y} = \alpha.\frac{\partial^2 T}{\partial y^2} \tag{3}$$

The corresponding steady flow equations are given in (1)

The initial and boundary conditions are :

$$\begin{array}{lll}
u = 0 & : & T = T_{\infty} \quad \text{at} \quad x = 0 \\
u = v = 0 & : & \text{for all values of } y \text{ and } t < 0 \\
u = v = 0 & : & \text{for } y = 0 \text{ and } t \geqslant 0 \\
u = 0 & : & \text{for } y \to \infty \text{ and } t \geqslant 0 \\
T = T_{\infty} & : & t < 0 \\
T = T_w & : & \text{at } y = 0 \text{ and } t = 0+ \\
T = T_{\infty} & : & \text{as } y \to \infty \text{ and } t \geqslant 0
\end{array} \tag{4}$$

Integration of equation (2) with respect to y from 0 to δ and use of equation (1) gives

$$\frac{\partial}{\partial t}\int_0^{\delta} u.\ dy + \frac{\partial}{\partial x}\int_0^{\delta} u^2\ dy = -\nu\left(\frac{\partial u}{\partial y}\right)_{y=0} - \frac{\sigma \beta^2{}_{\delta}}{\rho_{\infty}}\int_0^{\delta} u.\ dy$$

$$+ \beta g\ \frac{\partial}{\partial x}\left[(T_w - T_{\infty})\int_0^{\delta} dy \int_y^{\delta} \frac{T - T_{\infty}}{T_w - T_{\infty}}\ dy\right] \tag{5}$$

Assuming

$$\theta = \frac{T - T_{\infty}}{T_w - T_{\infty}}\ ;\ T_w - T_{\infty} = A.\ x^a \tag{6}$$

Equation (3) can be written as

$$\frac{\partial \theta}{\partial t} + u.\frac{\partial \theta}{\partial x} + v.\frac{\partial \theta}{\partial y} + \frac{au\ \theta}{x} = \alpha\frac{\partial^2 \theta}{\partial y^2} \tag{7}$$

which when integrated with respect to y from 0 to δ yields

$$\frac{\partial}{\partial t}\int_0^{\delta} \theta.\ dy + \frac{\partial}{\partial x}\int_0^{\delta} u.\ \theta.\ dy = -\alpha\left(\frac{\partial \theta}{\partial y}\right)_{y=0} \frac{a}{x}\int_0^{\delta} \theta\ u.\ dy \tag{8}$$

We assume simple profiles for u and θ satisfying the boundary condition (4). They are

$$u = u_1(x, t).\frac{y}{\delta}(1 - y/\delta)^2 \tag{9}$$

$$\theta = \theta_1(x, t).\quad (1 - y/\delta)^2 \tag{10}$$

Substitution of equations (9) and (10) in the equations (5) and (8) leads to

$$\frac{\delta}{12} \cdot \frac{\partial u_1}{\partial t} + \frac{1}{105} \frac{\partial}{\partial x} (u_1^2 \delta) = - \frac{\nu u_1}{\delta} - \frac{\sigma B^2 u_1 \delta}{12 \rho_\infty} + \frac{\beta g A}{12} \frac{\partial}{\partial x} (x^a \delta^2 \theta_1) \tag{11}$$

$$\frac{\delta}{3} \cdot \frac{\partial \theta_1}{\partial t} + \frac{1}{30} \cdot \frac{\partial}{\partial x} (u_1 \theta_1 \delta) = \frac{2 \alpha \theta_1}{\delta} - \frac{a u_1 \theta_1 \delta}{30 x} \tag{12}$$

with the boundary conditions

$$u_1 = 0 \; ; \; \theta_1 = 1 \text{ at } t = 0+ \tag{13}$$

Introducing the transformations

$$\begin{aligned} \tau &= \frac{Gr^{2/5} . \nu}{L} \cdot \frac{t}{x^s} \\ u_1 &= \frac{10 \nu \, Gr^{2/5} \, x^r \, F(\tau)}{L} \\ \theta_1 &= \frac{10}{\sqrt{6}} \, G(\tau) \\ B &= \left(\frac{N \rho_\infty \nu}{\sigma L} \right)^{\frac{1}{2}} Gr^{1/5} \, x^q \\ \delta &= \sqrt{6} \, L^{\frac{1}{2}} \, x^m / Gr^{1/5} \end{aligned} \tag{14}$$

where Gr is the Grashof number $\frac{A B g L^{5/2}}{\nu^2}$ and N is the interaction parameter based on the characteristic velocity $(BgA\nu^{\frac{1}{2}})^{2/5}$ and the characteristic length $L = (\nu^2/\beta g A)^{2/5}$ Equations (11) and (12) become

$$x^{m+r-s} F' + \frac{2}{7} x^{2r+m-1} \{(r + m) F^2 - s \tau F F'\} + 2 \, x^{r-m} F + N x^{2q+r+m} F$$
$$- x^{a+2m-1} \{(a + 2m) G - s \tau G'\} = 0 \tag{15}$$

and

$$x^{m-s} G' + \{(r F - s \tau F') G - s \tau F G' + m F G\} x^{m+r-1}$$
$$+ a \, x^{r+m-1} F G - \frac{1}{P_r} x^{-m} G = 0 \tag{16}$$

where P_r is the Prandtl number and prime denotes differentiation with respect to τ.

For similarity solution to be possible, the following relations must be satisfied

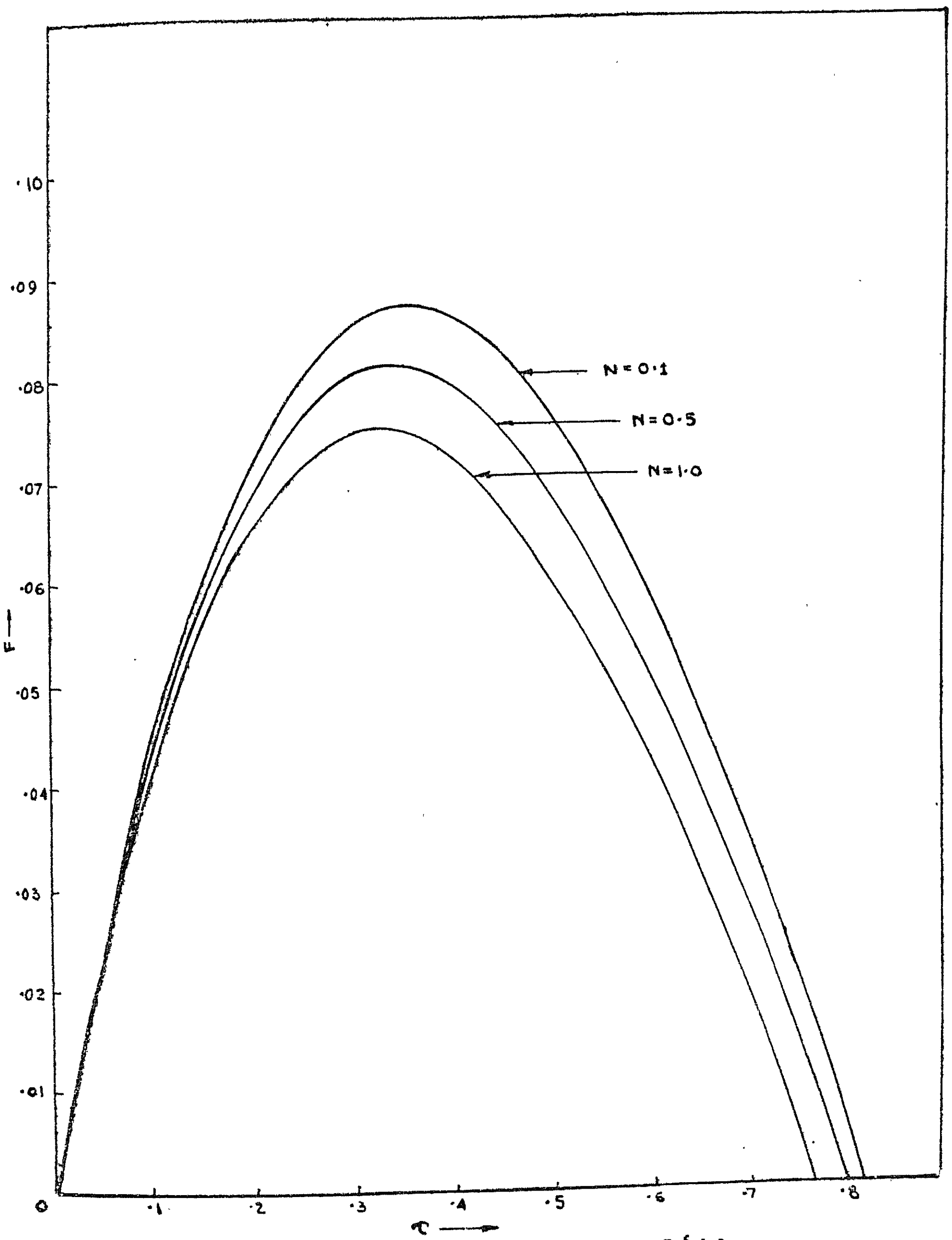
$$m + r - s = 2r + m - 1 = r - m = 2q + r + m = a + 2m - 1$$

and

$$m - s = m + r - 1 = -m$$

which yield

$$m = \tfrac{1}{5} (2 - a), \; s = \tfrac{2}{5} (2 - a), \; r = \tfrac{1}{5} (2a + 1) \text{ and } q = \tfrac{1}{5} (a - 2) \tag{17}$$



VARIATION OF "F" WITH τ FOR N = 0·1 , 0·5 & 1·0

Similarity solutions of the equations (15) and (16) for any value of 'a' and the corresponding values of m, s, r and q except the value $a = 2$ can be obtained. We have, however, solved them for the particular case when $a = -\frac{1}{2}$. The equations (15) and (16) for $a = -\frac{1}{2}$ become

$$F' - \tfrac{16}{7}\tau F F' + \tfrac{4}{7} F^2 + (2 + N) F - \tfrac{1}{2} G + \tau G' = 0 \tag{18}$$

$$(1 - \tau F) G' - \left(\tau F' + \frac{1}{P_r} \right) G = 0 \tag{19}$$

The boundary conditions are

$$F(o) = 0 \text{ and } G(o) = 1 \tag{20}$$

3. **Solution and Results** : Equations (18) and (19) under the boundary conditions (20) have been solved on IBM 7044 digital computor at I. I. T. Kanpur (India) for $P_r=1$. The results are shown in the table below. G does not depend appreciably on the interaction parameter. The curves in the Fig. are drawn for F for the values of N equal to 0·1, 0·5 and 1·0.

	$N = 0{\cdot}1$		$N = 0{\cdot}5$		$N = 1{\cdot}0$	
τ	F	G	F	G	F	G
0·00	0 000000	1·000000	·00000	1·000000	·000000	1·00000
0·05	0·023097	1·051883	·022869	1·051875	·022589	1·051865
0·10	0·042495	1·107554	·041667	1·107491	·040662	1·107416
0.15	0·058302	1·167016	0·56615	1·166813	·054600	1·166573
0·20	0·070584	1·230210	·067885	1·229752	·064706	1·229214
0·25	0 079396	1·296996	·075628	1·296144	·071253	1·295165
0·30	0·084823	1·367143	·080017	1·365759	·074518	1·364198
0·35	0·086988	1·440333	·081251	1·438296	·074777	1·436038
0·40	0·086090	1·516182	·076584	1·513404	·072341	1·510377
0·45	0·082394	1·594270	·075316	1·590711	·067536	1·586897
0·50	0·076223	1·674176	·068782	1·668950	·060706	1·665290
0·55	0·067933	1·755510	·060333	1·750483	·052183	1·745273
0·60	0·057890	1·837930	·050312	1·832313	·042285	1·826594
0·65	0·046441	1·921152	·039040	1·915091	·031300	1·909038
0 70	0·033904	2·004946	·026806	1·998611	·019480	1·992422
0·75	0·020555	2·089133	·013855	2·082707	·007042	2·076593
0·80	0·006628	2·173570	·000397	2·167243	– ·005835	2·161421

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Finite Bending of Plates—V

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1. Introduction

In parts I to IV [1-4] the problems of rectangular and circular blocks bent into shells have been solved on the basis of linear stress-strain relations.

During the last two decades the problems of incompressible rectangular and circular blocks bent into shells have been solved by various authors [5-9] and solutions obtained in terms of a general strain energy function. Various references are found in surveys by Green and Zerna [10] and Green and Adkins [11].

Recently, Green and Adkins [12] solved the problem of bending of an aelotropic cuboid into a right circular cylindrical shell and obtained a solution in terms of a general strain energy function. In this paper the problem of bending of an aelotropic incompressible circular block bent into an ellipsoidal shell has been considered. The solution has been obtained in terms of a general strain energy function. The case of a circular block bent into a spherical shell has been obtained as a particular case.

2. *Notation and formulae*

We adopt the notation and formulae of Green and Zerna [10] and Green and Adkins [11].

Let x^i be the initial, y^i the final and θ^i the curvilinear coordinates of the strained body, with g_{ij} and G_{ij} as metric tensors for the coordinate system θ^i in the unstrained and strained states of the body respectively. Then the covariant strain tensor ν_{ij} is given by

$$2\nu_{ij} = G_{ij} - g_{ij} \qquad 2{\cdot}1$$

The strain energy W of a homogeneous aelotropic body is expressed as a polynomial

$$W = W(e_{ij}) \qquad 2{\cdot}2$$

in the components of strain e_{ij}, where

$$e_{rs} = \frac{\partial\theta^i}{\partial x^r}\frac{\partial\theta^j}{\partial x^s}\,\nu_{ij} \qquad 2{\cdot}3$$

The stress tensor T^{ij} for a compressible body is given by

$$T^{ij} = \frac{1}{2\sqrt{I_3}} \left(\frac{\partial W}{\partial e_{rs}} + \frac{\partial W}{\partial e_{sr}} \right) \frac{\partial \theta^i}{\partial x^r} \frac{\partial \theta^j}{\partial x^s} \qquad 2{\cdot}4$$

where $\qquad I_3 = | 2e_{rs} + \delta_{rs} |$

For an incompressible body,

$$I_3 = 1$$

and

$$T^{ij} = \tfrac{1}{2} \left(\frac{\partial W}{\partial e_{rs}} \frac{\partial W}{\partial e_{sr}} \right) \frac{\partial \theta^i}{\partial x^r} \frac{\partial \theta^i}{\partial x^s} + pG^{ij}, \qquad 2{\cdot}5$$

where p is a scalar function of θ^i, and G^{ij} is the contravariant metric tensor of the curvilinear coordinates θ^i in the deformed body.

The equations of equilibrium, in the absence of body forces, are

$$T^{ij} \|_j = 0 \qquad 2{\cdot}6$$

the double line denoting convariant differentiation with respect to the curvilinear coordinates θ^i in the deformed body.

The physical components of stress σ_{ij} are given by

$$\sigma_{ij} = \left(\frac{G_{ii}}{G_{jj}} \right)^{\frac{1}{2}} G_{jm}\, T^{im}. \qquad 2{\cdot}7$$

3. *Bending of an incompressible aelotropic circular block into an ellipsoidal shell*

Suppose that in the undeformed state of the body it is a circular block bounded by the planes $x_3 = a_1$, $x_3 = a_2$ $(a_2 > a_1)$ and the cylinder $x_1^2 + x_2^2 = a^2$. The block is then bent symmetrically about x_3 axis into a part of an ellipsoidal shell, whose inner and outer boundaries are the ellipsoides of revolution obtained by revolving the confocal ellipses

$$x_3 = c \cosh \xi \cos \eta,\ x_1 = c \sinh \xi \sin \eta, \quad \xi = \xi_i \quad (i = 1, 2)\,; \qquad 3{\cdot}1$$

about the x_3 axis respectively and the edge $\eta = \alpha$. Let the y_i – axis coincide with x_i – axes and the curvilinear coordinates θ_i in the deformed state be a system of orthogonal curvilinear coordinates (ξ, η, φ), where φ is the angle between $y_1 y_3$ plane and the plane through a point in the space and y_3 – axis.

Then

$$y_1 = c \sinh \xi \sin \eta \cos \varphi, \quad y_2 = c \sinh \xi \sin \eta \sin \varphi, \quad y_3 = c \cosh \xi \cos \eta. \qquad 3{\cdot}2$$

Since the deformation is symmetric about y_3 – axis, we see that

(*i*) the planes x_3 = constant in the undeformed state become the ellipsoidal surfaces ξ = constant in the deformed state,

(*ii*) the curves $x_1^2 + x_2^2$ = constant in the undeformed state become the circles η = constant in the deformed state,

(*iii*) $\tan^{-1} \dfrac{x_2}{x_1} = \varphi$.

These imply that

$$x_3 = f(\xi), \quad (x_1^2 + x_2^2)^{\frac{1}{2}} = F(\eta), \quad x_1 \tan \varphi = x_2 \qquad 3{\cdot}3$$

which give

$$x_1 = F(\eta)\cos\varphi, \quad x_2 = F(\eta)\sin\varphi, \quad x_3 = f(\xi). \tag{3·4}$$

The metric tensors for the strained and the unstrained state of the body are given by

$$G_{ij} = \begin{bmatrix} c^2(\cosh^2\xi - \cos^2\eta) & 0 & 0 \\ 0 & c^2(\cosh^2\xi - \cos^2\eta) & 0 \\ 0 & 0 & c^2\sinh^2\xi\sin^2\eta \end{bmatrix} \tag{3·5}$$

$$g_{ij} = \begin{bmatrix} f'^2 & 0 & 0 \\ 0 & F'^2 & 0 \\ 0 & 0 & F^2 \end{bmatrix}$$

where $$f' = \frac{df}{d\xi}, \text{ and } F' = \frac{dF}{d\eta}. \tag{3·6}$$

The condition of incompressibility

$I_3 = 1$ gives

$$\frac{c^3(\cosh^2\xi - \cos^2\eta)\sinh\xi}{f'} = \frac{FF'}{\sin\eta} \tag{3·7}$$

In this equation, the variables ξ and η can be separated only if η is so small that $\cos\eta$ can be replaced by unity. Physically this implies that the maximum value of η, which is approximately equal to the ratio of the circular block in the deformed state to the semi–axis of the ellipsoidal shell in the direction of the y_3-axis, measured in radians, is a small quantity. This, however, does not mean that the displacements $y_1 - x_1$, $y_2 - x_2$, $y_3 - x_3$ are all small.

Then (3·7) can be written as

$$\frac{c^3\sinh^3\xi}{f'} = \frac{FF'}{\eta} = A, \tag{3·8}$$

where A is an arbitrary constant.

Then $$x_3 = f(\xi) = \frac{c^3}{A}\int \sinh^3\xi\, d\xi + \beta \tag{3·9}$$

$$= \frac{c^3}{A}\left(\frac{\cosh^3\xi}{3} - \cosh\xi\right) + B \tag{3·10}$$

and

$$x_1^2 + x_2^2 = F^2(\eta) = A\eta^2 + D, \tag{3·11}$$

where B, D are constants.

As the internal and external boundaries of the ellipsoidal shell are given by $\xi = \xi_i$, $i = 1, 2$) respectively which were initially the planes $x_3 = a_1$, $x_3 = a_2$, (3·10) gives

$$a_i = \frac{c^3}{A}\left(\frac{\cosh^3\xi_i - 3\cosh\xi_i}{3}\right) + B, \quad i = 1, 2. \tag{3·12}$$

Solving these equations, we get

$$A = \frac{c^3}{(a_2 - a_1)} \left\{ \frac{\cosh^3 \xi_2 - \cosh^3 \xi_1}{3} - (\cosh \xi_2 - \cosh \xi_1) \right\} \qquad 3{\cdot}13$$

$$B = \frac{a_2 \left(\frac{\cosh^3 \xi_1}{3} - \cosh \xi_1 \right) - a_1 \left(\frac{\cosh^3 \xi_2}{3} - \cosh \xi_2 \right)}{\frac{\cosh^3 \xi_1 - \cosh^3 \xi_2}{3} - (\cosh \xi_1 - \cosh \xi_2)} \qquad 3{\cdot}14$$

Since the bending is symetric about the x_3 – axis, we must have $x_1^2 + x_2^2 = 0$ when $\eta = 0$. Then (3·11) gives

$$x_1^2 + x_2^2 = F^2(\eta) = A\eta^2. \qquad 3{\cdot}15$$

After substituting (3·10) and (3·15) in (3·5) and (3·6) we get

$$G_{ij} = \begin{bmatrix} (c \sinh \xi)^2 & 0 & 0 \\ 0 & (c \sinh \xi)^2 & 0 \\ 0 & 0 & \eta^2 (c \sinh \xi)^2 \end{bmatrix} \qquad 3{\cdot}16$$

$$G^{ij} = \begin{bmatrix} \frac{1}{(c \sinh \xi)^2} & 0 & 0 \\ 0 & \frac{1}{(c \sinh \xi)^2} & 0 \\ 0 & 0 & \frac{1}{\eta^2 (c \sinh)^2} \end{bmatrix} \qquad 3{\cdot}17$$

$$g_{ij} = \begin{bmatrix} \frac{(c \sinh \xi)^6}{A^2} & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & A\eta^2 \end{bmatrix} \qquad 3{\cdot}18$$

$$g^{ij} = \begin{bmatrix} \frac{A^2}{(c \sinh \xi)^2} & 0 & 0 \\ 0 & \frac{1}{A} & 0 \\ 0 & 0 & \frac{1}{A\eta^2} \end{bmatrix} \qquad 3{\cdot}19$$

From (2·1), (2·3), (3·16), (3·17), we get

$$\frac{\partial x^r}{\partial \theta^s} = \begin{bmatrix} 0 & F' \cosh \varphi & -F \sin \varphi \\ 0 & F' \sin \varphi & F \cos \varphi \\ f' & 0 & 0 \end{bmatrix} \qquad 3{\cdot}20$$

$$\frac{\partial \theta^r}{\partial x^s} = \begin{bmatrix} 0 & 0 & \frac{1}{f'} \\ \frac{\cos \varphi}{F'} & \frac{\sin \varphi}{F'} & 0 \\ \frac{-\sin \varphi}{F} & \frac{\cos \varphi}{F} & 0 \end{bmatrix} \qquad 3{\cdot}21$$

From (2·1), (2·3), (3·16) to (3·21), the strain tensors ν_{ij} and e_{ij} are given by

$$2\nu_{11} = \left(c^2 \sinh^2 \xi - \frac{c^6 \sinh^6 \xi}{A^2} \right), \qquad 3{\cdot}22$$
$$2\nu_{22} = (c^2 \sinh^2 \xi - A),$$
$$2\nu_{33} = \eta^2 (c^2 \sinh^2 \xi - A),$$
$$\nu_{12} = \nu_{23} = \nu_{31} = 0.$$

$$2e_{11} = \frac{c^2 \sinh^2 \xi}{A} - 1,$$

$$2e_{22} = \frac{c^2 \sinh^2 \xi}{A} - 1,$$

$$2e_{33} = \frac{A^2}{c^4 \sinh^4 \xi} - 1, \qquad 3{\cdot}23$$

$$e_{12} = e_{21} = e_{31} = 0.$$

Also, from (2·5) and (3·23), we obtain the components of the stress tensor

$$T^{11} = \frac{A^2}{c^6 \sinh^6 \xi} \left(\frac{\partial w}{\partial e_{33}} \right) + \frac{p}{c^2 \sinh^2 \xi},$$

$$T^{22} = \frac{1}{A} \left(\frac{\partial w}{\partial e_{11}} \right) + \frac{p}{c^2 \sinh^2 \xi},$$

$$T^{33} = \frac{1}{A\eta^2} \left(\frac{\partial w}{\partial e_{11}} \right) + \frac{p}{\eta^2 c^2 \sinh^2 \xi}. \qquad 3{\cdot}24$$

The non-zero Christoffel symbols are given by

$$\Gamma^1_{11} = \Gamma^2_{21}\, \Gamma^3_{31} = \cosh \xi, \; \Gamma^1_{22} = - \cosh \xi, \; \Gamma^1_{33} = - \eta^2 \cosh \xi. \qquad 3{\cdot}25$$

The equations of equilibrium (2·6) with the help of (3·25) reduce to

$$\frac{\partial T^{11}}{\partial \xi} + \coth \xi \, (4\, T^{11} - T^{22} - \eta^2 T^{33}) = 0, \qquad 3{\cdot}26$$

and the other two equations being satisfied identically.

Substituting (3·24) in (3·26) we get

$$\frac{\partial T^{11}}{\partial \xi} = \frac{\coth \xi}{c^2 \sinh^2 \xi} \left[\frac{2c^2 \sinh^2 \xi}{A} \frac{\partial w}{\partial e_{11}} - \frac{2A^2}{c^4 \sinh^4 \xi} \frac{\partial w}{\partial e_{33}} \right]$$
$$- \frac{2 \coth \xi}{c^2 \sinh^2 \xi} \left[\frac{A^2}{c^4 \sinh^4 \xi} \frac{\partial w}{\partial e_{33}} + p \right] \qquad 3{\cdot}27$$

Now
$$\frac{\partial W}{\partial \xi} = \frac{\partial W}{\partial e_{11}} \frac{\partial e_{11}}{\partial \xi} + \frac{\partial W}{\partial e_{22}} \frac{\partial e_{22}}{\partial \xi} + \frac{\partial W}{\partial e_{33}} \frac{\partial e_{33}}{\partial \xi}$$

$$= \coth \xi \left[\frac{2c^2 \sinh^2 \xi}{A} \frac{\partial W}{\partial e_{11}} - \frac{2A^2}{c^4 \sinh^4 \xi} \frac{\partial W}{\partial e_{33}} \right] \tag{3·28}$$

Substituting (3·28) in (3·27) we get

$$\frac{\partial T^{11}}{\partial \xi} = \frac{1}{c^2 \sinh^2 \xi} \frac{\partial W}{\partial e_{33}} - \frac{2 \coth \xi}{c^2 \sinh^2 \xi} \left[\frac{A^2}{c^4 \sinh^2 \xi} \frac{\partial W}{\partial e_{33}} + p \right] . \tag{3·29}$$

Again from (3·24) and (3·29) we obtain

$$\frac{\partial p}{\partial \xi} = \frac{\partial W}{\partial \xi} + \frac{4 A^2 \cosh \xi}{c^4 \sinh^5 \xi} \frac{\partial W}{\partial e_{33}} - \frac{A^2}{c^4 \sinh^4 \xi} \frac{\partial}{\partial \xi} \left(\frac{\partial W}{\partial e_{33}} \right) \tag{3·30}$$

which gives on integration

$$p = W + W_0 - \frac{A^2}{c^4 \sin^4 \xi} \left(\frac{\partial W}{\partial e_{33}} \right), \tag{3·31}$$

where W_0 is a constant.

From (2·7), (3·24) and (3·31) we get

$$\sigma_{11} = W + W_0,$$

$$\sigma_{22} = \sigma_{33} = W + W_0 + \frac{c^2 \sinh^2 \xi}{A} \left(\frac{\partial W}{\partial e_{11}} \right) - \frac{A^2}{c^4 \sinh^4 \xi} \left(\frac{\partial W}{\partial e_{33}} \right), \tag{3·32}$$

Boundary conditions

If the inner boundary of the shell $\xi = \xi_i$ is free from traction, we must have

$$\sigma_{11} = 0 \quad \text{where} \quad \xi = \xi_1$$

which on substitution in (3·32) gives

$$W_0 = - W(\xi_1).$$

On the outer surface of the shell $\xi = \xi_2$, we have to apply a normal traction R given by

$$R = \sigma_{11}(\xi_2) = W(\xi_2) - W(\xi_1). \tag{3·33}$$

On the edge $\eta = \alpha$ the distribution of tranctions between φ and $\varphi + d\varphi$ give rise to a force F and a couple of moment M about the origin given by

$$F = \alpha \int_{\xi_1}^{\xi_2} \sigma_{22} \, (c \sinh \xi)^2 \, d\xi, \tag{3·34}$$

$$M = \alpha \int_{\xi_1}^{\xi_2} \sigma_{22} \, (c \sinh \xi)^2 \, (c \cosh \xi) \, d\xi. \tag{3·35}$$

Substituting (3·32) in these equations, we get

$$F = \alpha \int_{\xi_1}^{\xi_2} \left[(W + W_0) \, c^2 \sinh^2 \xi + \frac{c^4 \sinh^4 \xi}{A} \left(\frac{\partial W}{\partial e_{11}} \right) - \frac{A^2}{c^2 \sinh^2 \xi} \left(\frac{\partial W}{\partial e_{33}} \right) \right] d\xi. \tag{3·36}$$

$$M = \alpha \int_{\xi_1}^{\xi_2} \left[(W+W_0)\, c^3 \sinh^2 \xi \cosh \xi + \frac{c^5 \sinh^4 \xi \cosh \xi}{A} \left(\frac{\partial W}{\partial e_{11}} \right) - \frac{A^2 \cosh \xi}{c^2 \sinh^2 \xi} \left(\frac{\partial W}{\partial e_{33}} \right) \right] d\xi, \tag{3·37}$$

which can be integrated when the strain energy function W is specified.

4. *Particular case*

Bending of an aelotropic incompressible circular block into a spherical shell :

If $c \cosh \xi_i = c \sinh \xi_i$ in (3·1) we get the case of a circular block bent into a spherical shell, so that

$$\xi \to \infty \ , \quad c \to 0, \quad \text{and } c \cosh \xi,\ c \sinh \xi \to r, \tag{4·1}$$

and consequently the orthogonal curvilinear coordinates (ξ, η, φ) are replaced by the spherical polar coordinates (r, θ, φ). Then equations (3·32), (3·36) and (3·37) reduce to

$$\sigma_{11} = W + W_0,$$

$$\sigma_{22} = \sigma_{33} = W + \quad + \frac{r^2}{A} \left(\frac{\partial W}{\partial e_{11}} \right) - \frac{A^2}{r^4} \left(\frac{\partial W}{\partial e_{33}} \right), \tag{4·2}$$

$$F = \alpha \left[\frac{(W+W_0)\, r_2^{\,2} - r_1^{\,2})}{2} + \int_{r_1}^{r_2} \frac{r^2}{A} \left(\frac{\partial W}{\partial e_{11}} - \frac{A^3}{r^6} \frac{\partial W}{\partial e_{33}} \right) r\, dr \right],$$

$$M = \alpha \left[\frac{(W+W_0)\ (r_2^{\,3} - r_1)}{3} + \int_{r_1}^{r_2} \frac{r^2}{A} \left(\frac{\partial W}{\partial e_{11}} - \frac{A^3}{r^6} \frac{\partial W}{\partial e_{33}} \right) r^2\, dr \right] \tag{4·4}$$

Thus, to bend an aelotropic circular block into a part of an ellipsoidal shell, we require a resultant F and a couple M on the edge together with a normal force R on its outer surface.

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